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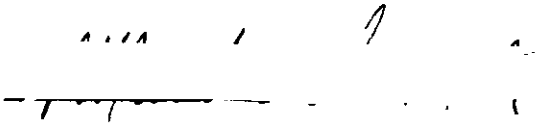

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THE EFFECT OF SOLVENT ON THE RATES OF RACEMIZATION AND DISSOCIATION OF THE FERROUS TRIS-(PHENANTHROLINE) ION

A THESIS

Presented to

The Faculty of the Graduate Division

by

Francis Marshall Van Meter, Jr.

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THE EFFECT OF SOLVENT ON THE RATES OF RACEMIZATION AND DISSOCIATION OF THE FERROUS TRIS-(PHENANTHROLINE) ION

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SUMMARY

The purpose of the present investigation was to study the effect of solvent on the rate of racemization of $Fe(phen)_3^{2+}$. The racemization rate constants were determined in water, methanol, acetone, formamide, N,N-dimethylformamide, ethylene glycol, glycerol, acetonitrile, and acetic acid, and in mixtures of water with methanol, acetone, formamide, N,N-dimethylformamide, ethylene glycol, glycerol, urea, and ethylene carbonate. The dissociation rate constants were determined in water, methanol, acetone, formamide, N,N-dimethylformamide, acetonitrile, and acetic acid, and in mixtures of water with methanol, acetone, formamide, and N,N-dimethylformamide. In all cases the dissociation rates were much slower than the racemization rates and it is felt that racemization is preponderantly intramolecular in all of these solvents.

The solubilities of $Fe(phen)_3(ClO_4)_2$ and naphthalene were determined in all of the pure solvents mentioned above, in pure dimethylsulfoxide, and in mixtures of water with methanol, acetone, and N,N-dimethylformamide.

The racemization rate constants appear to be related to the solubility of the complex perchlorate, the solvent dielectric constant, and the solvent viscosity by the equation: $\log(k) = -3.25 - 0.506\left[\log\left(\frac{\eta}{S_{complex}}\right) + \frac{87.9}{D}\right]$. The solubilities of the complex perchlorate and naphthalene are related by the equation: $\log(S_{complex}) = -\frac{87.9}{D} + 1.42 + 0.955 \log(S_{naphth.})$. These two equations are consistent with one another in derivation and in that the same coefficient of the dielectric term appears

both equations.

It is suggested that the solvent's effect on the racemization rates is due to preferential solvation of the ligands on the $Fe(phen)_3^{2+}$ ion by solvents that exhibit a high solvating power for naphthalene, and to viscous resistance of the solvent to reorganization in the vicinity of the ion.

The solvent effects on dissociation rates are suggested to be preferential solvation of the leaving ligands and the solvent's ability to act as a replacing ligand.

Ion association was found to have a retarding effect on the rates of racemization of $Fe(phen)_3^{2+}$.

The compound, $Fe(phen)_3(ClO_4)_2$ was found to crystallize from water as the anhydrous salt rather than as the dihydrate which had been previously suggested.

The NMR chemical shifts of the 5,6 protons on $Fe(phen)_3^{2+}$ are reported for water, methanol, acetone, N,N-dimethylformamide, acetonitrile, dimethylsulfoxide, and for mixtures of water with acetone and N,N-dimethylformamide.

The compound, $Fe(phen)_3(ClO_4)_2$ was found to undergo rapid oxidation to the corresponding Fe(III) complex in glacial acetic acid by nitrogen(IV) species in the presence of nickel perchlorate, perchloric acid, sulfuric acid, or metaphosphoric acid. This oxidation does not occur in water at similar oxidant concentrations or in the other solvents. The reaction appears to be due to a shift in the redox potentials of either the $Fe(phen)_3^{2+}$ -$Fe(phen)_3^{3+}$ couple or the N(III)-N(IV) couple.

CHAPTER I

INTRODUCTION

The effects of solvent on reaction rates and mechanisms are considerable. Different solvents may lead to orders of magnitude differences in reaction rates, and competing mechanisms may be suppressed or enhanced. For example, solvents of high polarity will enhance the rate of a reaction proceeding by an ionic dissociation mechanism while solvents of low polarity will suppress such a mechanism.

The interest in solvent effects on reactions has led to the publication of a book on the subject[1]. Books on kinetics and mechanisms of reactions often include a section on solvent effects. A series of articles on solvent effects on ions and reactions is currently being published[37]. An understanding of solvent effects on reaction rates and mechanisms is significant to our basic understanding of chemical processes and in a practical sense is useful for optimizing commercial preparative processes.

Previously, treatment of solvent effects on reactions has tended to concentrate on calculation of the electrostatic solvation energies of the various species involved. Given the solvent dielectric constant and knowing the nature of the species involved in the reaction, the electrostatic solvation energies of the reactants and of the activated complex may be calculated. From the differences of these numbers the electrostatic solvation contribution to the activation energy may be evaluated. It must be emphasized at this point that any charged species in a solvent will have

an electrostatic solvation energy associated with it, but that reaction rates are concerned with the difference in the energies of the reactants and of the activated complex. There is not necessarily a difference in the solvation energy of the reactants and the activated complex. Thus, an ion in solution may react with no electrostatic solvation contribution to the activation energy.

The electrostatic treatment has been applied to ion-ion, ion-dipole, and dipole-dipole reactions. In addition to the dielectric constant, correlations with other parameters which may provide a better indication of the microscopic dielectric properties of a solvent than the macroscopic dielectric constant have been made[2,3,4,5].

A solvent cage effect has also been noted[6], wherein different diffusion rates in different solvents may limit the ease with which a reactant species may interact with species other than its nearest neighbors. This effect is generally treated as part of the frequency factor in the transition state model.

In outer sphere electron exchange reactions, the solvent effect on the electronic potential barrier for the electron exchange is involved with the solvent dielectric constant in a complicated way[7]. For inner sphere electron exchange reactions, the treatment follows the electrostatic solvation energy approach.

Lewis, Coryell, and Irvine[17] have investigated the $Co(en)_3^{2+}$ - $Co(en)_3^{3+}$ electron transfer in water and compared it with the predictions of the Marcus, Zwolinski, Eyring theory[18,19]. Silverman and Dodson[20] have done the same for some Fe(II) - Fe(III) systems. Calculated and experimental free energies of activation differed by a few Kcal.

Substitution reactions on several transition metal complexes have been investigated in non-aqueous solvents. The substitution of chloride in cis-$Co(en)_2Cl_2^+$ by NO_3^-, Cl^-, Br^-, or NCS^- in methanol appears to be by an S_N1 mechanism[8] similar to the situation in water. Several other Co(III) complexes behave similarly in methanol, dimethylsulfoxide, N,N-dimethylformamide, and tetramethylenesulfone[9,10,11,12,13,14,15,16]. The reactions all appear to be complicated by ion pairing effects, but the evidence suggests that an S_N1 mechanism is generally operative. Reaction rates are reported to be not much different from those in water, and no interpretations of the solvent effects on rates are made.

In dimethylsulfoxide, cis-trans isomerization of $Co(en)_2Cl_2^+$ has been shown to occur by two paths: one is a dissociation involving loss of a chloride ion, and the other is a direct intramolecular rearrangement[34,35,36].

Racemization rates of $Ni(bipy)_3^{2+}$, $Ni(phen)_3^{2+}$, $Fe(bipy)_3^{2+}$, $Fe(phen)_3^{2+}$, and $Cr(ox)_3^{3-}$ have been investigated in solvents other than water (bipy = 2,2'-bipyridine; phen = 1,10-phenanthroline; ox = oxalate).

Davies and Dwyer[21] suggested that since the Arrhenius equation parameters for racemization of the Ni(II) complexes appeared to be independent of solvent, an intramolecular process was indicated. Wilkins and Williams[22], however, measured both racemization and dissociation rates and found the rates to be experimentally the same, indicating racemization by dissociation.

Seiden, Basolo, and Neumann[23] measured the rates of racemization and dissociation of $Fe(bipy)_3^{2+}$ and $Fe(phen)_3^{2+}$ in methanol-water mixtures and found racemization rates to be appreciably faster than dissociation.

This evidence suggests that the Fe(II) complexes favor intramolecular racemization in organic solvents. Accurate determination of the rates of racemization was difficult because of the rapid rates in methanol containing solutions and the large absorbancies of the compounds in the regions of the spectrum normally used for polarimetry.

The acid dependence of the rate of racemization of $Fe(bipy)_3^{2+}$ in water suggests that a partial dissociation mechanism may be operative here[24]. In this mechanism only one end of the bipyridine ligand comes loose from the iron atom, the other nitrogen atom remaining bonded to it. Since rotation may occur around the iron-nitrogen bond before the free nitrogen atom becomes reattached, racemization may occur.

In the $Fe(phen)_3^{2+}$ system, the ligands are constrained by the steric rigidity of the ring system to remain nearly planar. Inspection of Fisher-Hirschfelder models indicates that both nitrogen atoms in phenanthroline must be coordinated at the same time. Racemization of $Fe(phen)_3^{2+}$ in water is acid independent which supports this conclusion.

Schweitzer and Rose[25] have measured the racemization rates for $Cr(ox)_3^{3-}$ in mixtures of water with methanol, ethanol, isopropanol, dioxane, and acetone. The rates all decrease with increasing organic component in the solvent. The mechanism is thought to be dissociative. Very little speculation is made as to the role of the solvent in the reaction.

Davies and Dwyer[21] compared solvent viscosities with racemization rates in the Ni(II) systems, and Basolo, et al.[23] considered both viscosity and volume shrinkage on mixing of the solvent in the Fe(II) systems. No positive conclusions can be drawn from these results. In general,

little interpretation of these solvent effects has been attempted.

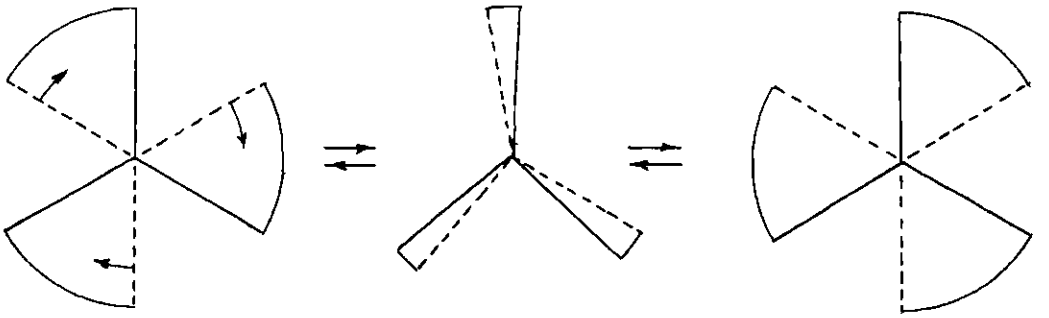
The $Fe(phen)_3^{2+}$ system is interesting in that the rate of racemization is strongly dependent on the solvent composition. Basolo, et al.[23] indicate almost a hundredfold increase in rate on going from water to methanol. The racemization in water at 25° C was found to be 89 percent intramolecular[24] and the percentage increased as the methanol content of the solvent increased[23].

Three detailed mechanisms for intramolecular (non-dissociative) racemization of "octahedral" tris-chelates have been proposed[26]. Probably the simplest of these is the Bailar twist[27,28,29]. It is a twisting motion along the threefold axis of the molecule in the same manner as a variable pitch propeller reverses pitch. The molecule passes through a transition state having D_3h symmetry.

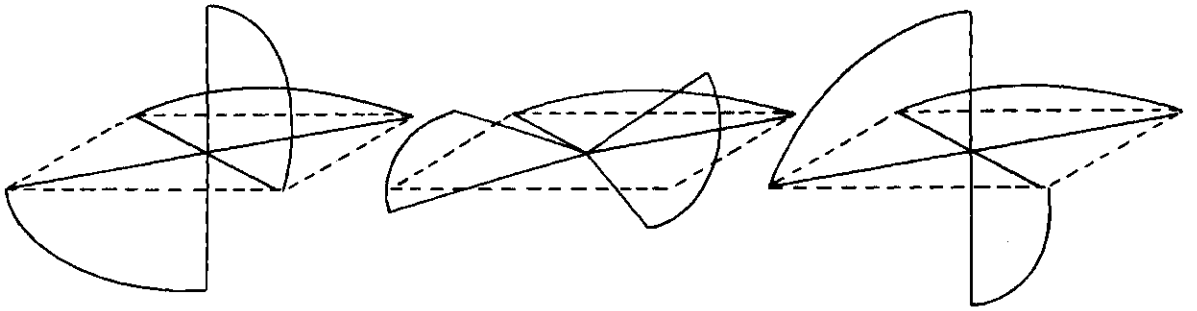
Another mechanism, the Rây and Dutt mechanism[30], involves motion of two ligands around the twofold axis bisecting the third ligand. The transition state has C_2v symmetry.

The third mechanism, the Springer and Sievers mechanism[26], involves rotation of two of the ligands around the same twofold axis bisecting the third ligand but in the opposite direction from the Rây and Dutt mechanism. The transition state has D_3h symmetry.

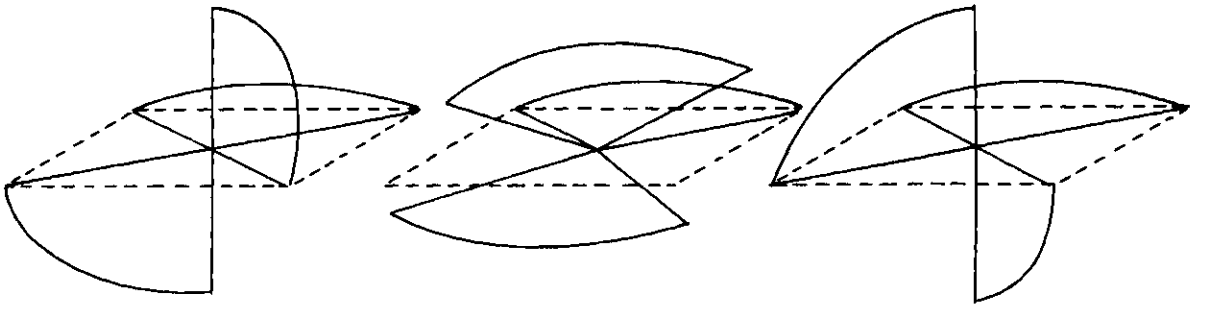
Presently there is no definitive way of establishing which of the mechanisms is operative for complexes involving symmetrical bidentate ligands. For unsymmetrical ligands an NMR method has been proposed[31]. For symmetrical ligands, measurements of the volume of activation for racemization has been suggested and applied to solid $Fe(phen)_3(ClO_4)_2$. The results are of doubtful significance.



The Bailar Twist



The Ray and Dutt Twist



The Springer and Sievers Twist

Chart of the Three Proposed Intramolecular Racemization Mechanisms for Octahedral Tris-Chelates

Inspection of Fisher-Hirschfelder models suggests that the Rây and Dutt mechanism would encounter the least steric hindrance. Both other mechanisms pass through the D_3h transition state where steric hindrance between the different ligands at the two and eight positions is large. All three pass through an approximately trigonal prismatic ligand field so that the ligand field energy should not be greatly different between the three mechanisms. Thus, the Rây and Dutt mechanism seems favorable on the basis of simple arguments, although this is by no means certain.

Regardless of which of the three proposed mechanisms best describes the racemization of $Fe(phen)_3^{2+}$, only a small solvent effect due to electrostatic solvation energy is expected. No formal separation of charges occurs in any of the mechanisms. The only electrostatic solvation energy change as the ion passes through the activated complex should be due to the change in the size of the ion. The measured volume of activation for racemization of solid $Fe(phen)_3(ClO_4)_2$ is -1.0 cm^3/mole[32,33]. The volume of the complex ion is estimated to be about 1500 cm^3/mole based on reasonable bond lengths and angles and the ion being spherical. The effective change in the radius of the ion is thus about 2×10^{-4} of the radius. Little effect on the electrostatic solvation energy is expected from a change in ionic radius this small. This conclusion is open to criticism as the solid state volume of activation was used and the ion was assumed to behave as a sphere. The negative volume of activation implies contraction of the ion on activation which is contrary to chemical intuition. An investigation of the effect of solvent polarity on the racemization rate of $Fe(phen)_3^{2+}$ would show whether electrostatic solvation of an expanding or contracting ion played an important role in racemization of

the ion.

Comparison of the rates of racemization and dissociation of $Fe(phen)_3^{2+}$ in several solvent systems would indicate whether or not the increasing ratio of racemization rate to dissociation rate on going from water to methanol solvent as observed by Basolo, et al.[23] is a general feature of this ion in aqueous-organic solvents. Consideration of both racemization and dissociation rates as a function of solvent composition might lead to conclusions about the factors influencing rates that might not come to light if only one reaction were studied. Measurement of both rates would give the intramolecular racemization rates.

If solvent polarity were found not to be a factor in the solvent dependence of the rates, then other factors which might lead to solvent dependence of the rates could be investigated. This would be significant for two reasons: first, previously unobserved solvent-solute interactions might be revealed and their influence on rates could be investigated; and second, the validity of using electrostatic solvation energy treatments and ignoring other possible factors in treating solvent effects on rates might be assessed by comparing the magnitude of solvent effects in the absence of electrostatic solvation effects on the rate with reactions where electrostatic solvation effects are known to be a factor in the rates.

The purpose of this investigation is to provide answers to some of the above questions and to study factors such as solvent parameters, solubilities, NMR chemical shifts, and other properties which may influence the rates of racemization and dissociation.

CHAPTER II

EXPERIMENTAL

Chemicals

The 1-10-phenanthroline monohydrate was obtained from Matheson, Coleman, and Bell and was used as received.

Ferrous chloride tetrahydrate was obtained from Matheson, Coleman, and Bell and was recrystallized from aqueous hydrochloric acid prior to use.

The following chemicals were obtained as reagent grade and were utilized without further purification:

cobaltous nitrate hexahydrate
ethyl iodide
ferric nitrate nonahydrate
hydrochloric acid
magnesium metal turnings
magnesium nitrate hexahydrate
nickel nitrate hexahydrate
nitric acid
perchloric acid
potassium antimony tartrate hemihydrate
potassium nitrate
sodium hydroxide
sodium nitrate
sodium perchlorate monohyrate
stannous chloride dihyrate
sulfuric acid

Methyl isonicotinate was purchased from Aldrich Chemical Company

and was used as received.

Naphthalene was obtained from Matheson, Coleman, and Bell and was recrystallized from methanol. The melting point was 80.0° C (literature: 80.22° C, K_f = 68).

Nitric oxide and nitrogen dioxide were obtained in cylinders from The Matheson Company.

Anhydrous sodium perchlorate was obtained from Columbia Organic Chemicals Company and was redried by heating to 120° C under vacuum before each use.

Fisher Scientific Company SO-K-3 stabilized Karl Fischer reagent and SO-K-5 diluents were used.

Solvents

Water used in all solvents and preparations was distilled and stored in a glass bottle.

Methanol was Baker Chemical Company "defined purity" grade and was dried by refluxing and distilling from magnesium methoxide as has been described in the literature[49]. The distillate was stored in standard taper stoppered glass flasks. The distillate, when treated with magnesium metal, reacted immediately to give a clear solution with no gel or precipitate.

Acetone was Baker "analyzed" reagent, dried by treating with Drierite, filtering, and distilling. For mixtures of acetone with water, the treatment with Drierite was left out and the supplier's analysis for water (0.2 percent) was included in determining the solvent composition.

N,N-dimethylformamide obtained from Matheson, Coleman, and Bell

was treated with Drierite, filtered, distilled under vacuum (boiling point: 35-36° C at 10 mm. Hg), and stored in a glass stoppered bottle in a desiccator ($n_D^{24.7}$, 1.4304; literature n_D^{25}, 1.4294[38]). Fisher Scientific Company certified reagent dimethylformamide, reported to contain 0.00 percent water, was used in preparing the dimethylformamide-water mixtures.

Formamide obtained from Fisher Chemical Company was purified by vacuum distillation (boiling point 88° C at 5.5 mm. Hg). The initial and final 20 percent was discarded. The remainder was fractionally frozen to a melting point of 2.50° C (literature: 2.55° C, K_f = 3.50[39]). It was stored in standard taper glass stoppered flasks under nitrogen and in the dark.

Dimethylsulfoxide (Fisher certified reagent) was treated with Linde 4A molecular sieve and fractionally frozen twice. The melting point was 18.55° C (literature: 18.55° C[40]). It was stored in a dark glass bottle with a teflon gasket in the cap.

Glycerol (reagent, minimum purity 95 percent) was purified by distillation at reduced pressure, discarding the initial 30 percent and the final 20 percent (n_D^{25}, observed: 1.4736; literature: 1.4735[50]).

Ethylene glycol (Eastman Chemical Company, Eastman grade) was found to contain 0.2 percent water and was used as received.

Acetonitrile (Matheson, Coleman, and Bell spectroquality reagent; n_D^{30}, observed: 1.3411; literature: 1.3393[53]); density, observed: 0.7738 at 27° C, literature: 0.7745 at 27° C[53]) was used without further purification.

Ethylene carbonate (Eastman Chemical Company) was recrystallized prior to use.

Urea (Fisher "certified reagent") was used without further purification.

Mixed solvents were prepared and stored in glass stoppered volumetric flasks. The components were either weighed in the flasks on a single pan analytical balance or transferred into the flasks from 50, 10, and 5 ml Geissler burets. Both methods allowed a precision of 0.001 in the mole fraction of the solvent components.

In all cases solvents which had been stored for extended periods or opened repeatedly were discarded in favor of fresh solvents. Aqueous mixtures containing formamide, N,N-dimethylformamide, ethylene carbonate, or urea were prepared immediately before use. Solvents containing $NaClO_4$ were prepared immediately before use. All solvents were protected from direct exposure to the sunlight. All solvents were taken from freshly opened containers and kept in tightly capped glass containers.

Preparation of Compounds

Tris-(1,10-phenanthroline)-Iron(II) Perchlorate

This compound was prepared several times in the same manner.

Typically 1.00 g of $FeCl_2 \cdot 4H_2O$ was dissolved in 25 ml of water and 3.00 g of 1,10-phenanthroline hydrate in 25 ml of methanol was added to it. The mixture was heated on a steam bath, and 7.0 g of $NaClO_4 \cdot H_2O$ in 100 ml of water was slowly added. The resulting fine crystals of $Fe(phen)_3(ClO_4)_2$ were collected on a medium fritted glass filter, washed with cold water, and dried in a vacuum desiccator. With care nearly 100 percent yield could be achieved. If, however, the sodium perchlorate is rapidly added to a cold solution of $Fe(phen)_3^{2+}$ in water, a very fine

precipitate is produced which is difficult to filter.

1-Tris-(1,10-phenanthroline)-Iron(II) Perchlorate

This preparation is a variation on the procedure of Dwyer and Gyarfas[41] involving diastereoisomeric resolution with antimony d-tartrate (the formulation of this ion as antimonyl tartrate has been disputed[42]). Advantage is taken of the fairly fast racemization of $Fe(phen)_3^{2+}$ in hot water compared with the negligible rate for antimony d-tartrate to produce nearly 100 percent resolution of the d-l mixture into l-$Fe(phen)_3$ (antimony d-tartrate)$_2 \cdot 8H_2O$.

Typically 0.33 g of $FeCl_2 \cdot 4H_2O$ in 10 ml of water was treated with 1.00 g of 1,10-phenanthroline hydrate. To this mixture 1.2 g of potassium antimony d-tartrate hemihydrate in 10 ml of water was added. The solution and precipitate were heated to boiling, and water was added while maintaining the mixture near boiling until the precipitate was dissolved. The water was evaporated near 100° C until about 50 ml was left. The mixture was then allowed to cool and crystals of l-$Fe(phen)_3$(antimony d-tartrate)$_2 \cdot 8H_2O$ were collected on a filter. The rate of racemization of $Fe(phen)_3^{2+}$ in water at 100° C is rapid enough so that only the l-complex crystallizes. The solid does not appear to racemize appreciably at this temperature.

The solid $Fe(phen)_3$(antimony d-tartrate)$_2 \cdot 8H_2O$ was dissolved in cold aqueous NaOH, and a cold aqueous solution of $NaClO_4$ was added. An exceedingly fine precipitate of l-$Fe(phen)_3(ClO_4)_2 \cdot 3H_2O$ formed. The precipitate was washed twice with cold water by centrifuging and decanting the liquid layer. Finally the precipitate was washed with cold water and filtered. The filtration is slow and the filter was kept packed with ice to suppress dissolution of the complex. The filter cake was dried in a

vacuum desiccator. The l-$Fe(phen)_3(ClO_4)_2$ prepared in this manner had an optical activity comparable to that of material prepared by the method of Dwyer and Gyarfas[41] and was assumed to be of high optical purity.

Hexaaquonickel(II) Perchlorate

Twenty g of $Ni(H_2O)_6(NO_3)_2$ was dissolved in 50 ml of hot water, and 6.3 g of NaOH dissolved in 10 ml of water was added dropwise with vigorous stirring. The resulting precipitate was washed several times with hot water by centrifuging and decanting. The precipitate was then suspended in 100 ml of hot water and dissolved by adding 70 percent $HClO_4$ dropwise. The solution was filtered and slowly evaporated on a steam bath until crystals began to form. The solution was then slowly cooled to about 5° C and a four g crop of crystals was collected. Reheating to evaporate more solvent and cooling yielded a second crop of crystals. This second crop was later shown to be contaminated with nitrate ions and was not used. The extreme solubility of $Ni(H_2O)_6(ClO_4)_2$ and little change in solubility with temperature (222.5 g per 100 ml of water at 0° C, 273.7 g per 100 ml at 45° C) made recrystallization impractical. The $Ni(H_2O)_6(ClO_4)_2$ had to be kept over a drying agent in a desiccator due to its extreme hygroscopic nature.

1-Ethyl-4-Carbomethoxypyridinium Iodide

This compound was prepared by the method of Kosower[3]. Methyl isonicotinate (13.7 g) and ethyl iodide (17.0 g) in 50 ml of acetone were refluxed for eight hours and let set on ice overnight. The red-orange crystals were recrystallized from acetone and melted at 110° C (reported m.p. 111-112° C).

Tris-(1,10-phenanthroline)-Iron(III) Perchlorate

Approximately 0.5 g of $Fe(phen)_3Cl_2$ was prepared in situ in 50 ml of water from $FeCl_2 \cdot 4H_2O$ and 1,10-phenanthroline. Chlorine gas was bubbled through this solution until all of the red color was discharged. A solution of 1.0 g of $NaClO_4$ in 5 ml of water was added. The resulting blue precipitate was collected on a fritted glass filter, washed with cold water, and dried in a vacuum desiccator. The dry solid was stored in a desiccator. Prolonged contact with moist air or water led to reduction to the red Fe(II) complex.

Racemization Rates

Rates of racemization of l-$Fe(phen)_3(ClO_4)_2$ were measured in water, methanol, acetone, formamide, N,N-dimethylformamide, ethylene glycol, glycerol, acetonitrile, and acetic acid, and in mixtures of water with methanol, acetone, formamide, N,N-dimethylformamide, ethylene glycol, glycerol, urea, and ethylene carbonate. The dependence of the rate on complex concentration was studied in acetone, and also on addition of $NaClO_4$ in methanol, acetonitrile, N,N-dimethylformamide, acetone, and 0.8 mole fraction acetone in water.

In presenting the rates of a racemization reaction two points of view may be taken. One defines the rate constant operationally, thus:

$$k = \frac{1}{(\alpha - \alpha_\infty)} \frac{d}{dt} \quad ,$$

where α is the optical rotation at time t, and α_∞ is the optical rotation at infinite time. The other point of view defines the rate constant as the rate constant for the inversion process, thus:

$$k' = \frac{1}{[D]} \frac{d[D]}{dt} \quad ,$$

where [D] is the concentration of the D isomer. Normally the two rate constants are related to each other in the following way:

$$k = 2k' \quad .$$

In all cases we shall define our rate constants as k rather than as k′. This has the advantage of being more compatible with dissociation rates and is strictly defined in terms of experimental observables.

Initially, using a Bellingham and Stanley visual polarimeter graduated in increments of 0.02 degrees, it was not possible to observe significant rotations at either the mercury 546 nm or the sodium D lines. The highly absorbing solutions transmitted so little light that it was impossible to precisely match the light intensities in the half circles. If the solutions were made dilute enough that reproducible readings could be made, the angles of rotation were so small as to be useless for kinetic measurements. Measurement of the rotation of solutions with a Bendix Ericsson automatic polarimeter with an ETL NPL type 143A optical unit and a Texas Instruments Company model FWS strip chart recorder was attempted. Using an interference filter for the 546 nm Hg line, the instrument response was too slow to be usable and the output had a high noise level (± 10 percent of full scale) with solutions of l-$Fe(phen)_3(ClO_4)_2$ in the sample cell. In order to increase the transmitted light intensity, the filter was removed, and the red solution was allowed to act as its own filter. The response speed did not improve and the noise level went up. The lack of improvement was probably due to the broad band of wavelengths

transmitted by the solution in a region of the spectrum where a significant variation in rotation with wavelength is expected. The instrument functions by minimizing the intensity of the beam transmitted by the cell with a second polarizer and a Faraday cell. If the transmitted light is distributed over an appreciable range of rotary angle, the minimum in the photomultiplier output versus Faraday cell input becomes broadened and difficult to locate. In order to provide a high intensity beam and reasonable monochromaticity, the usual light source was removed and replaced by a tungsten lamp and housing removed from a Beckman DU spectrophotometer. A Corning colored glass filter having maximum transmittance at 610 nm was used in place of the 546 nm interference filter. Trial and error adjustment of the focusing and direction of the light beam gave an intensity approximately a hundred times that of the original light source. The 610 nm region is just outside the sharp increase in absorbance of the 510 nm band of $Fe(phen)_3^{2+}$ and just inside the cutoff region of the photomultiplier. With samples of l-$Fe(phen)_3(ClO_4)_2$ in the instrument, the response time was limited by the speed of the motor driving the potentiometer rather than the signal strength from the photomultiplier. Noise was about 2 percent of full scale on the ± 0.5 degree scale and 4 percent of full scale on the ± 0.1 degree scale. Only these two scales were used in racemization rate measurements.

The sample cell for racemization rate measurements was a water jacketed all pyrex glass cell with a 4.93 cm path length and a 7.35 ml sample volume. A brass ring was glued to one end of the cell jacket so that the cell could be clamped in an aluminum and brass block which held it in position in the polarimeter cell compartment.

Temperature control was provided by rapidly circulating water through the cell jacket. The temperature of the circulating water was controlled by a Precision Scientific Company L-10 temperature bath equipped with a Precision Scientific Company L-8 relay and a Philadelphia micro-set ± 0.01° C mercury thermometer. The measuring thermometer was a Sargent 76 mm mercury-in-glass thermometer graduated in tenths of a degree. It was calibrated against the freezing point of distilled water (0.00° C), and the sodium sulfate-sodium sulfate decahydrate-water triple point (32.38° C). Scale error was assumed to be linear over the range 0 - 40° C. The measuring thermometer was situated in the water flow just before it reached the sample cell. No detectable difference in temperature was noted when a similar thermometer calibrated in the same way was situated in the water flow just after it left the cell. Temperature control in the cell was better than ± 0.1° C. The major temperature control problem was probably heating or cooling of the sample as it was transferred from the thermostat bath to the sample cell. Experimentally this would show up as non-first order behavior of the decay of optical activity in the initial stages of the reaction. The results of runs in which this appeared to be the case were discarded.

For measurements below room temperature, the water returning to the thermostat was passed through a copper coil partially immersed in a bucket of ice. However, for measurements at 0° C the thermostat was partially filled with ice and the heater disconnected. During low temperature measurements dry nitrogen from a cylinder was passed through the cell compartment to prevent moisture from condensing on the cell windows.

For racemization rates, samples of l-$Fe(phen)_3(ClO_4)_2$ were

weighed into 10 ml vials. The solvent was thermostated directly in the thermostat bath prior to its use. The sample vial and a 10 ml syring with a 10 cm by 1.5 mm bore flat end stainless steel needle were thermostated in a tall beaker immersed in the bath and covered with a large cork. Solvent was drawn onto the syringe and transferred to the sample vial, then drawn back and forth between the vial and syringe until all of the sample had dissolved. The sample was then transferred to the sample cell with the syringe, and the cell was capped and placed in the polarimeter. A ground glass stopper with a small reservoir and a capillary opening to the outside prevented bubbles from getting into the sample cell.

For most runs two mg of complex was dissolved in 8.0 ml of solvent, giving a complex concentration of 3×10^{-4} molar. For runs where the complex concentration was varied, the complex was weighed to within 10^{-5} g on a Mettler microbalance, the rest of the procedure being the same. For very rapid rates the solid complex was placed in the sample cell before addition of the solvent. The sample was then dissolved by transferring it and the solvent from the cell to the syringe and back. For solutions containing added $NaClO_4$, weighed amounts of dried $NaClO_4$ were added to the solvent just before thermostating.

Optical rotation was followed as a function of time at such a chart speed that a half-life for racemization required about 4 inches of chart paper. For normal or rapid rates the optical rotation was followed for at least ten half-lives. The optical activity versus time curve was smoothed by using segments of plastic curves to draw a line approximating the average center of the excursions of the recorder in order to remove as much of the noise as possible. The angle of rotation was plotted

versus time on semi-logarithmic graph paper, and a best straight line was visually estimated through the data points. A typical racemization rate plot is presented in Figure 1.

For slower rates the recorder was stopped after four or five half-lives, and the value of the infinite time rotation angle was estimated. Using the size of the half-life determined by this estimated infinite time angle and the angle change in the last recorded half-life, a better value of the infinite time rotation angle was estimated. This cycle was repeated until essential agreement between successive values of the infinite time rotation angle was achieved. With practice, this procedure usually required only a few cycles.

For the very slow rates in glycerol, the rotation was followed for one or two half-lives, and the sample cell was removed from the polarimeter. Steam was passed through the cell jacket for about ten half-lives at 100° C based on an activation energy of at least 15 Kcal. The contents of the cell were then cooled to the thermostat temperature and an infinite time angle of rotation was measured.

Normal rates at temperatures above 15° C were reproducible within a few percent. For rapid rates and low temperatures, the disagreement increased to about 10 percent.

The individual measured rate constants for each run are recorded in Table 1. Table 2 gives the rate constants recorded in the study of the effects of complex concentration and $NaClO_4$ concentration. The rate constants are recorded to three significant figures without regard to the expected precision of the data. An inspection of the individual rate constants will indicate their reliability.

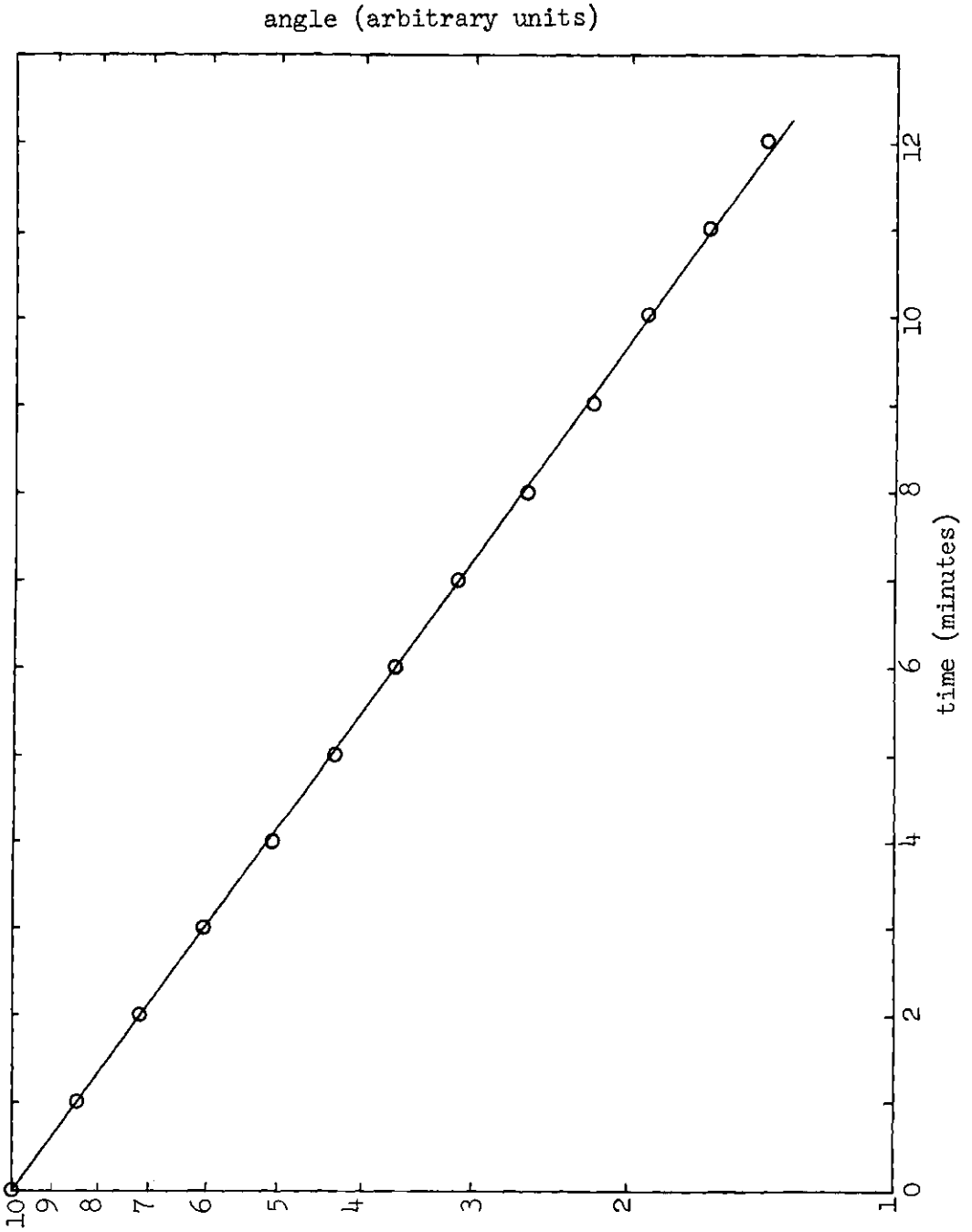


Figure 1. A Typical Rate Plot for Racemization in 0.6 Mole Fraction Acetone at 11.30°C.

Table 1. Experimental Rate Constants for Racemization of l-$Fe(phen)_3(ClO_4)_2$

Solvent comp.[a]	Temp. °C	10^4k, $sec.^{-1}$	Solvent comp.[a]	Temp. °C	10^4k, $sec.^{-1}$
Water			Methanol-Water (continued)		
1.000	12.00	0.695	1.000	24.90	187
1.000	15.20	1.40	0.500	18.80	34.3
1.000	18.80	2.20	0.100	12.00	1.40
1.000	24.90	6.50	0.200	12.00	2.70
1.000	24.90	6.53	0.201	12.00	2.75
1.000	35.60	33.2	0.300	12.00	4.53
Methanol-Water			0.400	12.00	7.12
0.100	24.90	11.5	0.406	12.00	7.37
0.200	24.90	20.8	0.500	12.00	10.8
0.300	24.90	32.2	0.501	12.00	11.2
0.400	24.90	53.2	0.600	12.00	16.3
0.500	24.90	71.7	0.600	12.00	16.8
0.600	24.90	102	0.700	12.00	23.8
0.700	24.90	133	0.700	12.00	26.4
0.800	24.90	190	0.800	12.00	31.2
0.900	24.90	212	0.800	12.00	31.9

(continued)

[a] Solvent composition is in mole fraction of the organic component.

Table 1. (Continued)

Solvent comp.[a]	Temp. °C	10^4k, sec.$^{-1}$	Solvent comp.[a]	Temp. °C	10^4k, sec.$^{-1}$
Methanol-Water (continued)			Acetone-Water[b]		
0.803	12.00	32.7	0.115	28.90	56.0
0.850	12.00	38.2	0.115	24.90	30.3
0.850	12.00	39.2	0.199	24.90	48.9
0.875	12.00	43.2	0.301	24.90	69.5
0.890	12.00	41.6	0.401	24.90	104
0.899	12.00	43.0	0.115	19.40	13.2
0.900	12.00	41.5	0.199	19.40	22.3
0.900	12.00	42.2	0.301	19.40	38.0
0.910	12.00	41.1	0.401	19.40	47.3
0.925	12.00	42.5	0.502	19.40	65.4
0.950	12.00	40.9	0.600	19.40	77.5
0.998	12.00	39.5	0.699	19.40	92.5
1.000	12.00	37.5	0.802	19.40	102
1.000	12.00	37.8	0.893	19.40	156
0.900	0.50	7.65	0.115	15.20	7.02
1.000	0.50	7.61	0.199	15.20	12.1
1.000	0.50	7.70	0.301	15.20	19.7

(continued)

[a] Solvent composition is in mole fraction of the organic component.

[b] See Table 2 for additional data on pure acetone.

Table 1. (Continued)

Solvent comp.[a]	Temp. °C	10^4k, sec.$^{-1}$	Solvent comp.[a]	Temp. °C	10^4k, sec.$^{-1}$
Acetone-Water[b] (continued)			Acetone-Water[b] (continued)		
0.401	15.20	29.8	0.802	7.10	18.3
0.502	15.20	36.3	0.893	7.10	24.5
0.600	15.20	43.7	0.900	5.47	23.7
0.699	15.20	55.0	0.900	0.15	9.02
0.802	15.20	59.0	N,N-dimethylformamide-Water		
0.893	15.20	117	0.100	13.87	6.07
0.119	11.30	7.09	0.100	19.07	14.0
0.301	11.30	11.0	0.100	22.89	25.2
0.401	11.30	16.3	0.100	27.39	48.8
0.502	11.30	22.5	0.200	11.07	7.50
0.600	11.30	27.5	0.200	14.26	12.4
0.699	11.30	33.6	0.200	16.78	19.2
0.802	11.30	34.4	0.200	19.92	31.7
0.900	9.45	37.7	0.300	9.50	12.7
0.502	7.10	11.4	0.300	14.00	23.0
0.600	7.10	14.2	0.300	17.87	43.7
0.699	7.10	17.0			

(continued)

[a] Solvent composition is in mole fraction of the organic component.

[b] See Table 2 for additional data on pure acetone.

Table 1. (Continued)

Solvent comp.[a]	Temp. °C	10^4k, sec.$^{-1}$	Solvent comp.[a]	Temp. °C	10^4k, sec.$^{-1}$
N,N-dimethylformamide-Water (con't.)			N,N-dimethylformamide-Water (con't.)		
0.300	22.18	89.5	0.800	5.10	37.5
0.400	0.15	4.68	0.800	5.10	38.4
0.400	5.47	11.5	0.800	9.95	74.6
0.400	9.50	21.3	0.800	9.95	78.0
0.400	14.00	43.3	0.800	14.52	133
0.500	0.17	8.87	0.800	14.55	134
0.500	5.47	17.8	1.000	0.70	20.8
0.500	9.45	33.0	1.000	0.70	21.4
0.600	0.30	10.1	1.000	5.10	42.1
0.600	0.30	10.1	1.000	5.10	43.2
0.600	5.10	25.9	1.000	9.95	103
0.600	5.10	26.1	1.000	9.95	104
0.600	9.95	49.2	1.000	14.52	163
0.600	9.95	52.6	1.000	14.55	166
0.600	14.52	102	Formamide-Water		
0.600	14.55	102	0.200	25.00	23.5
0.800	0.30	21.2	0.200	25.00	23.8
0.800	0.50	20.2			

(continued)

[a] Solvent composition is in mole fraction of the organic component.

Table 1. (Continued)

Solvent comp.[a]	Temp. °C	10^4k, sec.$^{-1}$	Solvent comp.[a]	Temp. °C	10^4k, sec.$^{-1}$
Formamide-Water (continued)			Ethylene Glycol-Water (con't.)		
0.400	25.00	34.6	0.993	21.36	8.05
0.400	25.00	34.6	0.993	21.36	8.15
0.600	25.00	49.1	0.125	25.20	10.6
0.600	25.00	49.8	0.125	25.20	10.5
0.800	25.00	61.5	0.248	25.20	13.7
0.800	25.00	62.1	0.248	25.20	13.8
1.000	25.00	58.3	0.375	25.20	14.9
1.000	25.00	58.3	0.375	25.20	15.4
1.000	25.00	59.7	0.496	25.20	16.9
1.000	25.00	60.0	0.496	25.20	17.0
			0.625	25.20	17.7
Ethylene Glycol-Water			0.625	25.20	16.9
0.248	21.36	7.37	0.745	25.20	16.7
0.248	21.36	7.37	0.745	25.20	16.9
0.496	21.36	9.10	0.875	25.20	15.5
0.496	21.36	9.29	0.875	25.20	16.6
0.745	21.36	9.22	0.993	25.20	15.5
0.745	21.36	9.25			

(continued)

[a] Solvent composition is in mole fraction of the organic component.

Table 1. (Continued)

Solvent comp.[a]	Temp. °C	10^4k, sec.$^{-1}$	Solvent comp.[a]	Temp. °C	10^4k, sec.$^{-1}$
Ethylene Glycol-Water (con't.)			Glycerol-Water (continued)		
0.993	25.20	15.4	0.300	25.00	5.17
0.248	30.23	28.4	0.500	25.00	2.95
0.248	30.23	28.6	0.500	25.00	3.20
0.496	30.23	35.0	0.700	25.00	1.75
0.496	30.23	35.0	0.835	24.77	0.995
0.745	30.23	33.8	0.835	24.77	1.07
0.745	30.23	33.9	0.835	24.80	0.945
0.993	30.23	31.9	0.835	30.20	2.90
0.993	30.23	32.0	0.835	33.76	5.39
			0.835	40.40	17.6
Glycerol-Water			1.000	25.00	0.779
0.100	24.42	6.35	1.000	25.00	0.798
0.100	26.47	8.96			
0.100	28.49	12.3	Acetonitrile		
0.100	31.65	19.7	1.000	25.00	147
0.100	35.51	36.3	1.000	25.00	149
0.300	25.00	4.70			

(continued)

[a] Solvent composition is in mole fraction of the organic component.

Table 1. (Continued)

Solvent comp.[a]	Temp. °C	$10^4 k$, $sec.^{-1}$	Solvent comp.[a]	Temp. °C	$10^4 k$, $sec.^{-1}$
Acetic Acid					
1.000	25.00	36.5			
1.000	25.00	37.7			
Urea-Water					
0.100	24.42	9.42			
Ethylene Carbonate-Water					
0.100	24.42	19.0			

[a] Solvent composition is in mole fraction of the organic component.

Table 2. Dependence of Rate Constants for Racemization on Complex Concentration and Added $NaClO_4$

$[NaClO_4]$	[complex]	$[ClO_4^-]$	$k \times 10^4$, $sec.^{-1}$
	Pure Acetone at 0.30° C		
0	0.00026	0.00052	80.8
0	0.00030	0.00060	60.9
0	0.00030	0.00060	74.0
0	0.00048	0.00096	61.0
0	0.00052	0.00104	63.2
0	0.00107	0.00214	60.0
0	0.00114	0.00228	55.6
0	0.00115	0.00230	61.2
0	0.00168	0.00336	42.2
0	0.00398	0.00796	20.2
0	0.00401	0.00802	22.3
0.00040	0.00030	0.00100	8.15
0.00040	0.00030	0.00100	8.94
0.00080	0.00030	0.00140	6.55
0.00080	0.00030	0.00140	6.65
0.00172	0.00027	0.00227	5.56
0.00410	0.00022	0.00454	4.35
0.00988	0.00022	0.01032	4.13

(continued)

Table 2. (Continued)

$[NaClO_4]$	[complex]	$[ClO_4^-]$	$k \times 10^4$, $sec.^{-1}$
	0.800 X Acetone at 11.56° C		
0.003	0.0003	0.034	31.0
0.121	0.0003	0.122	29.2
0.850	0.0003	0.851	20.8
	Pure Methanol at 25° C		
0.0061	0.0003	0.0067	190
0.0061	0.0003	0.0067	183
0.0183	0.0003	0.0189	178
0.0183	0.0003	0.0189	182
0.0426	0.0003	0.0432	179
0.0426	0.0003	0.0432	162
	Pure Acetonitrile at 25° C		
0.0058	0.0003	0.0064	93.6
0.0058	0.0003	0.0064	98.6
0.0175	0.0003	0.0181	96.4
0.0175	0.0003	0.0181	96.2
0.0407	0.0003	0.0413	91.0
0.0407	0.0003	0.0413	94.0

(continued)

Table 2. (Continued)

$[NaClO_4]$	[complex]	$[ClO_4^-]$	k x 10^4, $sec.^{-1}$
Pure N,N-dimethylformamide at 0.30° C			
0	0.0003	0.0006	19.1
0	0.0003	0.0006	21.8
0.0006	0.0003	0.0012	18.6
0.0006	0.0003	0.0012	18.8
0.0012	0.0003	0.0018	18.6
0.0012	0.0003	0.0018	18.8
0.0025	0.0003	0.0031	18.8
0.0025	0.0003	0.0031	19.1

Dissociation Rates

The rates of dissociation of $Fe(phen)_3(ClO_4)_2$ were measured in mixtures of water with methanol, acetone, N,N-dimethylformamide, and formamide, and also in acetic acid and acetonitrile.

The disappearance of $Fe(phen)_3^{2+}$ was followed at 510 nm with a Beckman DU spectrophotometer. The reaction involves the rate determining dissociation of one phenanthroline ligand from $Fe(phen)_3^{2+}$ followed by the rapid dissociation of the other two phenanthroline ligands[24]. A large excess of Ni(II) as $Ni(H_2O)_6(ClO_4)_2$ was used to react with the dissociated phenanthroline. This method has been described in the literature[23,44,45].

The temperature of the sample compartment of the spectrometer was controlled by circulating water from a Precision Scientific Company model C-1 thermostat bath regulated with a Philadelphia micro-set $\pm$ 0.01° C thermometer. The reactants and spectrophotometer cells were thermostated in a tall form beaker with a cork cover in a 10-gallon aquarium with a stirrer and a blade heater controlled by a relay and a Philadelphia micro-set $\pm$ 0.01° C thermometer. The regulator thermometers in each bath were set at 25.00° C with one of the calibrated thermometers described in the racemization rates section.

Sample cells were 1.00 cm glass stoppered silica cells.

Aliquots of an aqueous solution of $Ni(H_2O)_6(ClO_4)_2$ were pipetted into 10 ml volumetric flasks and the water was removed by heating for several hours to 90° C under a vacuum of less than 0.5 mm of Hg. Aliquots of $Fe(phen)_3(ClO_4)_2$ dissolved in acetone were pipetted into 10 ml vials and evaporated to dryness under vacuum at room temperature. The 10 ml

volumetric flasks with the nickel salt were filled with solvent and placed in the aquarium thermostat. The vials of $Fe(phen)_3(ClO_4)_2$ were placed in the tall beaker immersed in the aquarium thermostat. After equilibration, 5 ml of solvent was transferred to each vial with a glass pipet. The complex was dissolved in the solvent in each vial and the solutions were transferred to the spectrophotometer cells. Three different solvent samples and a reference cell with reacted complex and nickel salt in water were placed in the spectrophotometer and absorbance was recorded as a function of time. About twenty-five absorbance readings were taken on each sample before absorbance fell below 0.1. The absorbance versus time was plotted on semi-logarithmic graph paper and rate constants were determined from the slope of a visually estimated straight line through the data. The rate constants so determined were reproducible within about 2 percent, and the plots of log(absorbance) versus time were linear within the experimental precision of the data. A typical dissociation rate plot is presented in Figure 2.

The initial concentrations of the reactants in the dissociation rate measurements were: $Fe(phen)_3^{2+}$, 1.5×10^{-4} molar; Ni^{2+}, 1.5×10^{-2} molar.

The dissociations in acetic acid and acetonitrile were very slow and were followed for only approximately one-half-life.

Table 3 gives the individual experimental rate constants for the mixed solvents. The rate constant for acetonitrile is 2.03×10^{-6} $sec.^{-1}$, and for acetic acid it is 7.6×10^{-7} $sec.^{-1}$.

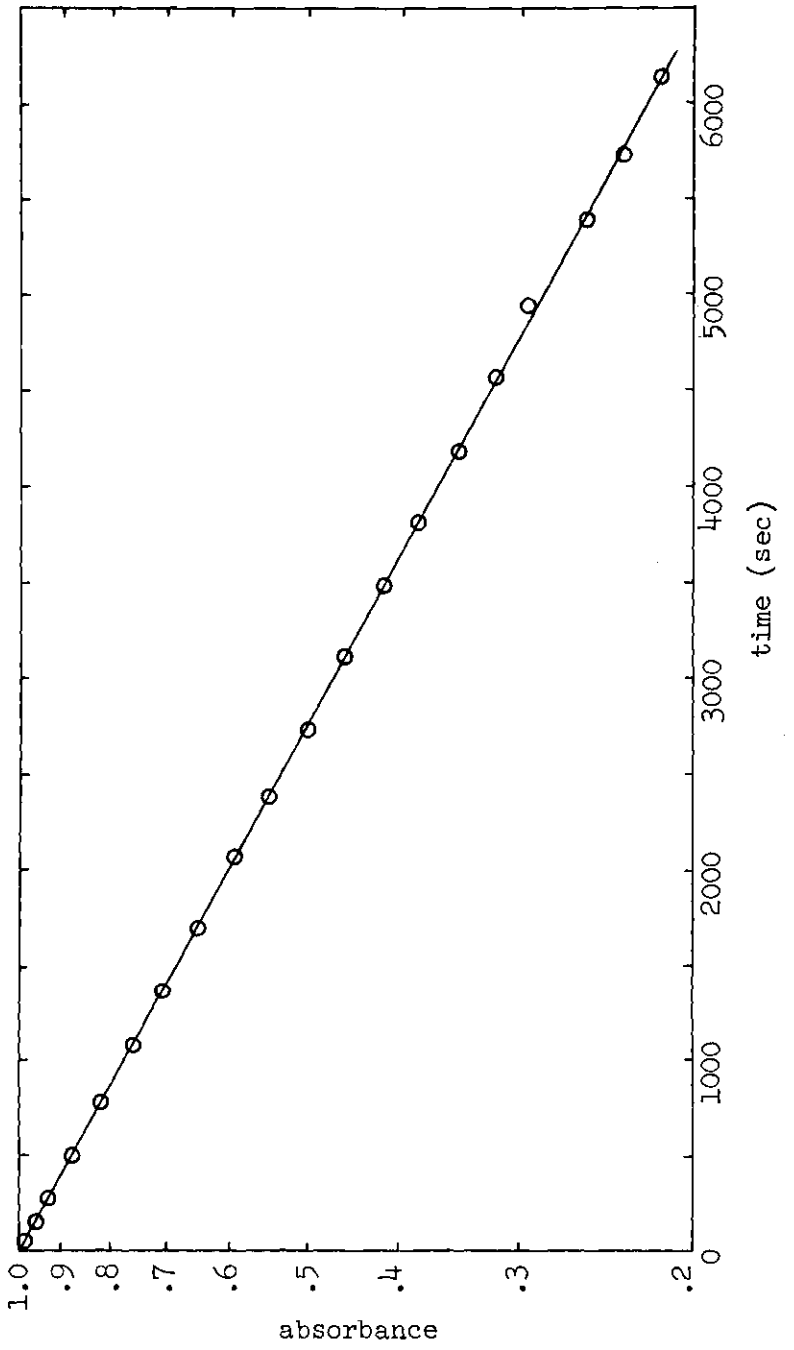


Figure 2. A Typical Rate Plot for Dissociation in 0.4 Mole Fraction Formamide at 25.00°C.

Table 3. Experimental Rate Constants[a] for Dissociation of $Fe(phen)_3(ClO_4)_2$ in Mixed Solvents at 25°C

Mole Fraction of the Organic Component					
0.000	0.200	0.400	0.600	0.800	1.000
		Methanol-Water			
0.776	0.92	1.61	2.31	2.28	0.40
0.770	0.98	1.66	2.38	2.33	
		Acetone-Water			
	1.52	2.57	3.11	2.42	0.060
	1.54	2.63	3.16	2.57	
		N,N-dimethylformamide-Water			
	2.44	4.45	5.20	4.44	2.37
	2.50	4.50	5.35	4.53	2.38
		Formamide-Water			
	1.88	2.49	2.50	2.13	1.83
	1.90	2.50	2.51	2.18	1.86

[a]Rate constants listed are k x 10^4, sec^{-1}

Solubilities of $Fe(phen)_3(ClO_4)_2$

The solubility of $Fe(phen)_3(ClO_4)_2$ was determined in water, acetone, acetonitrile, formamide, N,N-dimethylformamide, methanol, dimethylsulfoxide, glycerol, ethylene glycol, and in mixtures of water with acetone, methanol, and N,N-dimethylformamide at 25.00° C. The solubility in acetic acid was estimated but was not accurately determined.

Saturated solutions of $Fe(phen)_3(ClO_4)_2$ in the various solvents were prepared by adding the complex to 5 ml of solvent in a 10 ml ampoule at about 40° C until no more complex would dissolve. The ampoules were capped with rubber septum caps and attached to a small rack. The rack was suspended in the aquarium thermostat described in the section on dissociation rates. The ampoules were agitated by attaching a small motor with an eccentric weight on the shaft to the rack. This arrangement shook the ampoules vigorously enough to maintain the crystals of complex in suspension in the solutions.

Samples were withdrawn daily and the concentration of $Fe(phen)_3(ClO_4)_2$ measured spectrophotometrically. The shaking was stopped and the suspended crystals allowed to settle. About 0.5 ml of the liquid phase was withdrawn from each ampoule with a capillary pipet and used to fill a lambda pipet. The same lambda pipet was used for all measurements and was calibrated to contain 0.250 ml. Care had to be taken not to include any of the crystals of complex in the dark solutions withdrawn from the ampoules. The contents of the pipet were discharged and washed into appropriate size volumetric flasks. The flasks were filled with distilled water and samples withdrawn for analysis. The absorbance of each solution was measured at 510 nm on a Cary model 14 spectrophotometer in 1.00 cm

silica cells. A reference solution of 0.0632 mg of $Fe(phen)_3(ClO_4)_2$ per ml had an absorbance of 0.838 ± 0.003 in the 1.00 cm cells. The absorbance of the reference solution varied over a range of 0.006 in a random manner from day to day but the short-term reproducibility was 0.002 over an hour.

The solutions in glycerol and ethylene glycol had to be filtered before diluting for analysis since small crystals would not settle out of the viscous solvents. The samples were filtered through a small pipet with a medium fritted glass filter in the end before filling the 0.250 ml pipet.

After three consecutive determinations of solubility in a solvent gave essentially the same value, the last three values were averaged. On the last determination in some of the solvents the pipet was weighed before and after filling to give the density of the saturated solution.

Table 4 lists the experimental solubilities, average solubilities, and densities for the pure solvents, and Table 5 lists the values for mixtures of water with acetone, N,N-dimethylformamide, and methanol.

Solvent of Crystallization in $Fe(phen)_3(ClO_4)_2$

In order for the solubility studies to be meaningful, the nature of the solid in equilibrium with the solutions must be known. $Fe(phen)_3(ClO_4)_2$ crystallized from several solvents was investigated to see if solvent was included in a stoichiometric way in the crystal.

Pfeiffer and Werdelmann[43] had reported $Fe(phen)_3(ClO_4)_2$ to exist as the dihydrate. Their formula was based on a 3.8 mg weight gain in a P_4O_{10} moisture trap.

Three grams of $Fe(phen)_3(ClO_4)_2$ were recrystallized from water and air-dried.

Table 4. Solubilities of $Fe(phen)_3(ClO_4)_2$ in Various Pure Solvents at 25°C

Solvent	C_1[a]	C_2[a]	C_3[a]	$\overline{C}$[b]	$\overline{M}$[c]	d[d]	x[e]
Acetone	6.82	6.84	6.89	6.85	0.00861	0.7848	0.000643
Acetonitrile	84.4	82.8	82.0	83.1	0.104_4	0.8556	0.00552
Formamide	147	155	151	151	0.189_7	1.1648	0.00836
N,N-dimethylformamide	242	254	246	247	0.310_5	1.0500	0.0275
Methanol	2.28	2.18	2.38	2.28	0.00286	0.7868	0.000117
Water	0.697	0.691	0.691	0.693	0.000871	0.9972	0.0000158
Ethylene glycol	5.57	5.83	5.69	5.70	0.00716	1.1064	0.000404
Glycerol	2.25	2.35		2.30	0.00289	1.2532	0.000213
Dimethylsulfoxide	242	240	242	241	0.303	1.1626	0.0250
Acetic acid	0.16			0.16	0.00019	1.0436	0.000012

[a]Experimental solubility in grams per liter

[b]Average solubility in grams per liter

[c]Average solubility in moles per liter

[d]Experimental density of the saturated solution

[e]Average solubility in mole fraction of solute

Table 5. Solubilities of $Fe(phen)_3(ClO_4)_2$ in Mixed Solvents at 25°C

Solvent comp.[a]	C_1 g./l.	C_2 g./l.	C_3 g./l.	$\bar{C}$ g./l.	$\bar{M}$ mole/l.	d g./cm.^{3}
			Acetone-Water			
0.200	37.9	37.1	37.0	37.3	0.0459	0.9424
0.400	83.8	85.3	84.0	84.2	0.1060	0.9084
0.600	75.7	74.7	75.7	75.4	0.0952	0.8676
0.800	41.1	41.0	41.3	41.1	0.0516	0.8284
			Methanol-Water			
0.200	2.69	2.65	2.63	2.66	0.00334	
0.400	6.43	6.42	6.43	6.43	0.00809	
0.597	7.18	7.19	7.15	7.17	0.00902	
0.796	4.85	4.79	4.78	4.77	0.00600	
			N,N-dimethylformamide-Water			
0.100	8.92	8.87	8.81	8.87	0.01114	
0.200	37.7	38.5	38.4	38.2	0.0480	1.0052
0.500	150	151	151	151	0.1894	
0.600	180	183	182	182	0.228	
0.700	237	238	238	238	0.298	
0.800	256	258	258	257	0.322	1.0482
0.900	265	267	268	267	0.335	

[a]Solvent composition in mole fraction of the organic component

Three 0.2 g samples of the complex perchlorate were weighed into Coors 000 porcelain crucibles. The crucibles and samples were heated to 190° C for 20 hours in a drying pistol at 0.005 mm Hg pressure in the presence of anhydrous magnesium perchlorate. The crucibles were cooled under vacuum, removed, and weighed with a minimum exposure to the air. Table 6 lists the pertinent data on the weight loss of the complex perchlorate.

Two 0.1 g samples of $Fe(phen)_3(ClO_4)_2$ were dissolved in dried methanol, and the water present titrated with Karl Fischer reagent. The end points were observed electrically with an apparatus[46] which depends on the depolarization of platinum electrodes by free iodine. The titrant and methanol solvent were protected from atmospheric moisture by Drierite traps, and the titration cell was arranged so that samples could be dissolved and titrated without exposure to atmospheric moisture. The reference solution was 0.2519 g of distilled water in enough dried methanol to make 25.0 ml (10.08 mg H_2O per ml). Two blank titrations on the solvent methanol were made. Two standardization titrations on 1.00 ml samples of the reference solution were made. The titrant strength was 2.39 mg of water per ml of titrant. Two 0.1 g samples of $Fe(phen)_3(ClO_4)_2$ were dissolved and titrated. In blank, reference, and sample titration, the volume of solution titrated was 50 ml. Table 7 lists the water found in the complex.

Samples of solid $Fe(phen)_3(ClO_4)_2$ were crystallized from acetone, acetonitrile, formamide, and N,N-dimethylformamide. The crystals were dried of solvent adhering to the surface by tumbling on filter paper in a dry box. Potassium bromide pellets were made from two mg samples of each solid and 100 mg of KBr. The infrared spectra were run on a Perkin-

Table 6. Weight Loss on Drying of $Fe(phen)_3(ClO_4)_2$

Sample	Initial Weight, grams	Weight Loss, grams	Mole Ratio of H_2O to Complex
1	0.2171	0.0004	0.08
2	0.2051	0.0005	0.09
3	0.2084	0.0004	0.09

Table 7. Karl Fischer Water Found in $Fe(phen)_3(ClO_4)_2$

	Sample 1	Sample 2
Weight of sample	106.1 mg	102.6 mg
mg H_2O found	0.86 mg	0.88 mg
Weight percent H_2O	0.81	0.86
Moles of H_2O per mole of complex	0.36	0.38

Elmer model 237B grating infrared spectrometer. In the specimen from acetonitrile no band was observed in the region 2210-2260 cm^{-1}, and in the specimens from acetone, formamide, and dimethylformamide only weak carbonyl absorptions were observed in the 1650-1720 cm^{-1} region.

A preliminary X-ray structure investigation yielded unit cell parameters. A crystal of $Fe(phen)_3(ClO_4)_2$ was grown from aqueous solution, oriented on a precession camera, and mounted on a Picker full circle automatic diffractometer. h00, 0k0, and 00l reflections allowed the determination of the unit cell parameters. a was 35.743 Å, b was 15.918 Å, c was 11.642 Å, and beta was 77.68 degrees. The space group, as determined from systematic extinctions in the precession pictures, was Cc or C2/c. The calculated unit cell volume is 6782.8 cubic angstroms. With eight formula units per unit cell the calculated density of $Fe(phen)_3(ClO_4)_2$ is 1.5576 g/cm^3; and of $Fe(phen)_3(ClO_4)_2 \cdot H_2O$ is 1.5929. The measured density, by flotation in CCl_4 - $CHCl_3$ at 25° C, is 1.569 g/cm^3. The detailed solution of the crystal structure was eventually dropped.

Solubilities of Naphthalene

The solubility of naphthalene was determined at 25.00° C in water, acetone, acetonitrile, formamide, N,N-dimethylformamide, methanol, dimethylsulfoxide, ethylene glycol, glycerol, and acetic acid, and in mixtures of water with acetone, N,N-dimethylformamide, and methanol.

The method of determination was similar to that for the solubilities of $Fe(phen)_3(ClO_4)_2$.

Two maxima from the reported ultraviolet spectrum of naphthalene at 283 and 286 nm were selected for concentration measurement.

A reference solution of 0.256 mg per ml of naphthalene in 95 percent ethanol was scanned in 0.100 cm matched silica cells on the Cary 14 spectrophotometer. The maximum at 283 nm had an average absorbance of 0.748 and the maximum at 286 nm had an average absorbance of 0.758. The long-term precision of the instrument was 0.02 absorbance units, probably due to heavy use of the instrument including numerous changes of the potentiometer slidewires. The short-term precision, however, was 0.005 absorbance units. The absorbance scale was calibrated with the reference solution before each set of measurements.

Saturated solutions of naphthalene were prepared and thermostated in the same way as for $Fe(phen)_3(ClO_4)_2$. A 0.100 ml lambda pipet was used to measure aliquots of the saturated solutions. The aliquots were diluted with 95 percent ethanol and absorbance measured in 0.100 cm matched silica cells. For water, the solubility of naphthalene proved to be too small to measure in this way. A 100 ml volumetric flask of distilled water and 1.0 g of naphthalene flask was thermostated with the other samples. Quantities of this solution were filtered and the absorbance of naphthalene was measured in 5.00 cm matched silica cells without dilution. In all cases, the absorbancies were measured by scanning the 280-290 nm region slowly.

In some of the systems, the density of the saturated solutions were determined by weighing in a 0.250 ml lambda pipet. Three solubility measurements were made in each solvent.

Table 8 lists the solubilities in pure solvents, and Table 9 lists the solubilities in mixtures of water with acetone, N,N-dimethylformamide, and methanol.

Table 8. Solubilities of Napthalene in Various Pure Solvents at 25°C

Solvent	C_1[a]	C_2[a]	C_3[a]	$\overline{C}$[b]	$\overline{M}$[c]	d[d]	x[e]
Acetone	361	367	361	363	2.75	0.8776	
Acetonitrile	220	221	220	220	1.71_5	0.8368	
Formamide	6.78	7.00	6.96	6.91	0.0539	1.1320	
N,N-dimethylformamide	404	402	398	401	3.12	0.9828	
Methanol	74.8	74.4	73.6	74.3	0.579	0.8080	
Water	0.0298	0.0302	0.0299	0.0300	0.000234	0.9971	
Ethylene glucol	11.3	11.9	11.3	11.5	0.0896	1.1040	
Glycerol	1.36	1.35	1.34	1.35	0.0105_2	1.2528	
Dimethylsulfoxide	257	266	255	259	2.02	1.0750	
Acetic acid	113	113	113	113	0.882	1.0376	

[a]Experimental solubility in grams per liter

[b]Average solubility in grams per liter

[c]Average solubility in moles per liter

[d]Experimental density of the saturated solution

[e]Average solubility in mole fraction of solute

Table 9. Solubilities of Napthalene in Mixed Solvents at 25°C

Solvent comp.[a]	C_1 g./l.	C_2 g./l.	C_3 g./l.	$\bar{C}$ g./l.	$\bar{M}$ mole/l.	d g./cm^3
			Acetone-Water			
0.200	11.5	11.1	11.5	11.4	0.0890	0.9240
0.400	84.0	83.7	81.5	83.1	0.648	0.8804
0.600	190	188	189	189	1.47	0.8656
0.800	280	281	283	281	2.19	0.8648
			N,N-dimethylformamide-Water			
0.200	5.70	5.83	5.60	5.71	0.0445	0.9908
0.400	72.0	73.0	70.0	71.7	0.560	0.9800
0.600	167	167	166	167	1.30	0.9752
0.800	301	300	299	300	2.34	0.9748
			Methanol-Water			
0.200	0.266	0.264	0.264	0.265	0.00207	
0.400	2.59	2.60	2.61	2.60	0.0203	
0.597	11.5	11.5	11.6	11.5	0.0900	
0.796	32.6	34.4	34.5	33.8	0.264	

[a]Solvent composition in mole fraction of the organic component

Proton NMR of $Fe(phen)_3(ClO_4)_2$

The proton chemical shifts of the 5,6 protons on the ligands in $Fe(phen)_3(ClO_4)_2$ were measured in water, acetone, N,N-dimethylformamide, dimethylsulfoxide, acetonitrile, and methanol, and in mixtures of water with acetone and N,N-dimethylformamide. The dependence of the chemical shift on perchlorate ion concentration was measured in acetone.

Spectra were run on a Varian A-60D spectrometer and a Varian C-1024 time averaging computer. Filter bandwidth was 2.0 Hz, and RF field was 0.025 milligauss. Scan speed was 1 Hz per second and recorder speed was 2 mm per second. When the C-1024 computer was used, scan speed was 2 Hz per second, readout speed was 1 Hz per second, and chart speed was 2 mm per second. Fifty Hz scan widths were used with the C-1024 computer. Complex concentrations of 4 mg per ml could be scanned directly on the spectrometer. Lower concentrations required four to twenty scans with the C-1024 computer to give a measurable signal. Relative chemical shifts could be reproduced to within 0.3 Hz.

The reference signal was provided by including a sealed capillary of benzene in the sample tube. All chemical shifts are reported relative to the benzene signal. The same reference capillary was used in each measurement. This external reference system eliminates the solvent effect on the reference signal position and the reference compound's effect on the properties of the solvent which would exist with an internal reference.

Occasionally the reference tube would wobble in the spinning sample tube. This would give a broad reference signal with no ringing pattern and virtually eliminate the sample signal. Stopping and restarting the sample tube spinner usually eliminated this. A reference tube spinning

smoothly in the center of the sample tube gave a very sharp reference signal with pronounced ringing.

The concentration of $Fe(phen)_3(ClO_4)_2$ in the samples was 4.0 mg per ml except in water where it was limited to 0.6 mg per ml by the solubility. In acetone the complex concentration was varied between 0.75 and 6.00 mg per ml and $NaClO_4$ was added to some of the samples.

All spectra were recorded at the ambient temperature of the sample holder (36° C).

Tables 10, 11, and 12 list the experimental chemical shifts in the different solvents.

Measurements of Solvent Z-Values

Kosower[3] has made a list of solvent Z-values for the charge transfer band of 1-ethyl-4-carbomethoxypyridinium iodide. The Z-values for glycerol and ethylene glycol were not reported. The Z-value for the 1-methyl compound in ethylene glycol was reported, however. The Z-values for these two solvents with the 1-ethyl compound were measured by resolving the spectrum into Gaussian components.

The spectrum of 1-ethyl-4-carbomethoxypyridinium iodide was measured in each solvent in 1.00 cm silica cells on a Cary 14 spectrophotometer using pure solvent as a reference. The spectrum was slowly scanned from 450 nm down through the first aromtic band. Two concentrations were used, one for the c-t band and a lower concentration for the aromatic band. The charge transfer band appeared as a weak shoulder on the aromatic band, and the exact position of the maximum of the c-t band could not be located by inspection of the spectrum.

Table 10. Chemical Shifts of the 5,6 Protons of $Fe(phen)_3(ClO_4)_2$ in Various Solvents

Solvent	Chemical shift (Hz.)
Dimethylsulfoxide	107.9
Acetonitrile	84.3
Methanol	85.5

Table 11. Chemical Shifts of the 5,6 Protons of $Fe(phen)_3(ClO_4)_2$ in Acetone-Water and N,N-dimethylformamide-Water Mixtures[a]

Mole fraction of the organic component					
0.000	0.200	0.400	0.600	0.800	1.000
		Acetone-Water			
109.9	95.5	88.0	82.4	79.0	76.4
		N,N-dimethylformamide-Water			
109.9	102.6	100.1	97.8	96.1	96.2

[a] Chemical shifts in Hz (cycles per second).

Table 12. Dependence of the Chemical Shift of the 5,6 Protons of $Fe(phen)_3(ClO_4)_2$ in Acetone on Concentration and Added $NaClO_4$

$[Fe(phen)_3^{2+}]$[a]	$[NaClO_4]$[a]	$[ClO_4^-]$[a]	Chemical shift (Hz)
0.00094	0	0.00188	78.6
0.00189	0	0.00378	78.0
0.00377	0	0.00754	77.6
0.00754	0	0.0151	75.3
0.00377	0.00866	0.0162	75.4
0.00377	0.0203	0.0278	75.6
0.00377	0.0523	0.0599	75.4

[a] Concentration in moles per liter.

A computer program written by Schievelbein and Swart[48] was used to resolve the experimental spectrum into two Gaussian peaks. The input data were the absorbancies at various wavelengths, and trial values for the peak positions, heights, and widths. The program varied the peak parameters to get an improved fit of the calculated absorbancies with the experimental ones. The position of the aromatic band was fairly well defined and was held constant. The five other parameters were varied. There were forty-five measured values of the absorbance in each case. The refinement was stopped when the c-t band oscillated around one position and the change in position per cycle was less than 5 cm^{-1}.

The maximum in absorbance in ethylene glycol occurred at 29,475 cm^{-1}, giving a Z-value of 84.3 Kcal. The maximum in glycerol occurred at 28,553 cm^{-1}, giving a Z value of 81.6 Kcal.

Oxidation of $Fe(phen)_3^{2+}$ in Acetic Acid

The observation of dissociation in pure acetic acid was complicated by rapid oxidation of the $Fe(phen)_3^{2+}$ ion to the $Fe(phen)_3^{3+}$ ion. This occurred when nitrate ions were present as a contaminant in the $Ni(H_2O)_6(ClO_4)_2$ used to react with dissociated phenanthroline. Careful exclusion of nitrate ions solved the problem of measuring the rate of dissociation in acetic acid. A further investigation was begun to determine the cause of the disappearance of $Fe(phen)_3^{2+}$ when nitrate was present.

The disappearance of $Fe(phen)_3^{2+}$ in acetic acid was followed spectrophotometrically at 510 nm in the presence of nickel perchlorate and nitric acid. The absorbance remained essentially constant for an

induction period of up to several minutes and then decreased suddenly. This behavior was also observed with nickel perchlorate which was contaminated with nitrate ions. The decay of the absorbance approached an exponential decay in the final stages and eventually fell to a value essentially equal to that of a solution containing all of the components except the $Fe(phen)_3^{2+}$. With $Fe(phen)_3^{2+}$ concentration about 2×10^{-5} molar, HNO_3 concentration about 10^{-4} molar, and Ni^{2+} concentration about 10^{-3} molar, the induction period was several minutes. The induction period could not be reproduced within better than ± 30 percent. The disappearance of the red color of $Fe(phen)_3^{2+}$ was abrupt enough in relation to the induction period for the induction period to be observed visually. A number of experiments were carried out in which the induction period was visually observed.

Increasing the HNO_3 concentration to 5×10^{-4} molar reduced the induction period to a few seconds. Decreasing the HNO_3 concentration to 2×10^{-5} molar increased the induction period to about an hour. The induction period was insensitive to a fourfold change in the Ni^{2+} concentration.

Using $Fe(NO_3)_3 \cdot 9H_2O$ instead of HNO_3 led to the same general results with an induction period of several minutes for 2×10^{-4} molar Fe(III). Nickel(II) nitrate and cobalt(II) nitrate gave similar induction periods at approximately 10^{-3} molar. Potassium, sodium, and magnesium nitrate all gave induction periods of about two hours at the greatest concentration that could be achieved in acetic acid.

Exclusion of the nickel perchlorate prevented the disappearance of the $Fe(phen)_3^{2+}$ color until the HNO_3 concentration was increased to

approximately one molar. Perchloric acid, sulfuric acid, metaphosphoric acid (approximately HPO_3), and anhydrous magnesium perchlorate functioned in place of the nickel perchlorate with no difference in the results.

Initial absorbance of solutions of $Fe(phen)_3(ClO_4)_2$ and $Ni(H_2O)_6(ClO_4)_2$ in acetic acid were measured on a Cary 14 spectrophotometer. The color of the $Fe(phen)_3^{2+}$ ion disappeared when a trace of HNO_3 was added. Five ml of the colorless solution was diluted to 10 ml with water. The red color of the $Fe(phen)_3^{2+}$ returned, and absorbance measurements indicated that 98 percent of the original $Fe(phen)_3^{2+}$ had returned.

Simultaneous duplicate experiments involving equal concentrations of all reagents were performed where the induction period was observed visually. In one sample the HNO_3 was from a bottle which had been exposed to sunlight and was strongly colored with N_2O_4. In the other, the nitric acid was from a fresh bottle with no visible discoloration. The induction periods were significantly shorter with the discolored nitric acid.

A small vacuum line was constructed, to which cylinders of nitric oxide and nitrogen dioxide were attached. Pressure in the system was measured with a mercury manometer. A 10 ml ampoule containing 5 ml of acetic acid 2×10^{-5} molar in $Fe(phen)_3^{2+}$ and 10^{-2} molar in nickel perchlorate was attached to the system. The system was evacuated and flushed with nitrogen several times. The contents of the ampoule were agitated with a small magnetic stirring bar. When the solution was exposed to 100 mm Hg pressure of nitrogen dioxide, the color of the $Fe(phen)_3^{2+}$ disappeared instantly. When the system was evacuated and the solution was subsequently exposed to 100 mm of nitric oxide, the color of $Fe(phen)_3^{2+}$ reappeared instantly. As little as 5 mm of nitrogen dioxide caused

immediate disappearance of the red color. This was the smallest amount of the gas that could be reliably measured. Samples in which the color had been discharged with nitric acid and ferric nitrate were exposed to nitric oxide. In each case the color returned. A mixture of nitric oxide and nitrogen dioxide corresponding approximately to the formula N_2O_3 caused the return of the color to solutions previously treated with nitrogen dioxide.

A solution of 0.2 g of $Fe(phen)_3(ClO_4)_2$ in 1 ml of N,N-dimethylformamide was added dropwise to 50 ml of acetic acid containing 1.0 g of $Ni(H_2O)_6(ClO_4)_2$ and continuously saturated with nitrogen dioxide. Previous experiments had shown that although the solubility of $Fe(phen)_3(ClO_4)_2$ in acetic acid is only about 0.16 mg per ml, a metastable supersaturated solution lasts about 5 seconds before precipitation when the complex perchlorate is added in this manner. The result was a blue solution which deposited a blue precipitate after a few seconds. The intensity of the blue color in solution is about one hundredth of that of the red solution prior to reaction. After precipitation was complete, the remaining solution was light green in color (Ni(II)). When a sample of the green solution was added to water, only a light red color appeared. When a sample of the green solution and some of the blue solid were added to water, an intense red color appeared. At this time two formulas for the blue solid were suggested: $Fe(phen)_3(ClO_4)_3$ and $Fe(phen)_2(OAc)_2$.

Infrared spectra were run on samples of the blue precipitate and of authentic $Fe(phen)_3(ClO_4)_3$ in KBr pellets on a Perkin-Elmer 621 grating infrared spectrometer. The spectra were identical, but unfortunately the grinding operation in each case produced red KBr pellets, indicating that

the pellets now contained $Fe(phen)_3^{2+}$. This result might be expected for either $Fe(phen)_3(ClO_4)_3$ or $Fe(phen)_2(OAc)_2$ if moisture was present during the grinding.

A sample of the blue precipitate was carefully washed with acetic acid and vacuum dried. On dissolution in water, it produced a blue solution which changed slowly to red. The same behavior was observed for authentic $Fe(phen)_3(ClO_4)_3$. $Fe(phen)_3(X^-)_2$ species invariably disproportionate immediately in water to produce $Fe(phen)_3^{2+}$. Dissolving 0.0562 g of the blue precipitate in 50 ml of an acetone-water mixture containing 0.004 g of $SnCl_2 \cdot 2H_2O$ gave a solution having an absorbance of 0.576 at 510 nm in 0.100 cm cells. This indicated 99 percent of the iron and phenanthroline if the compound was $Fe(phen)_3(ClO_4)_3$, and 84 percent of the phenanthroline if the compound was $Fe(phen)_2(OAc)_2$. Added phenanthroline did not increase the absorbance.

The final test is an unusual one. Authentic $Fe(phen)_3(ClO_4)_3$ explodes when touched to a flame. $Fe(phen)_2(OAc)_2$ would only be expected to char. A 20 mg sample of the blue precipitate exploded when touched to a flame. Excluding the possibility of $Fe(phen)_2(ClO_4)_2$ or other perchlorate containing species, we feel that this establishes the blue precipitate as $Fe(phen)_3(ClO_4)_3$.

CHAPTER III

RESULTS

Rate Constants

Methanol-Water Mixtures

Figure 3 shows a typical plot of experimental rate constants versus mole fraction of the organic component of the solvent. The plot gives an indication of the reliability of the individual data points.

The curve in Figure 4 shows the variation of the rate constant for intramolecular racemization with X* methanol for methanol-water mixtures at 25° C. The intramolecular racemization rate constant is the difference between the racemization rate constant taken from an Arrhenius plot of data at each solvent composition and the dissociation rate constant at 25° C. The dissociation rate constants are interpolated from a plot of $k_{diss.}$ versus X methanol (Figure 8). Appendix B gives the numerical values for $k_{rac.}$, $k_{diss.}$, and $k_{int.rac.}$

The intramolecular racemization rate in water at 25° C is 5.63×10^{-4} $sec.^{-1}$ which is somewhat less than the value found by Basolo, Hayes, and Neumann[24] of 6.5×10^{-4} $sec.^{-1}$. Their measurement, however, was made in 1.0 molar HCl which may account for the difference. Dickens, Basolo, and Neumann[51] have reported that the racemization rate in water

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* The abbreviation X will be used here and throughout this paper to denote mole fraction.

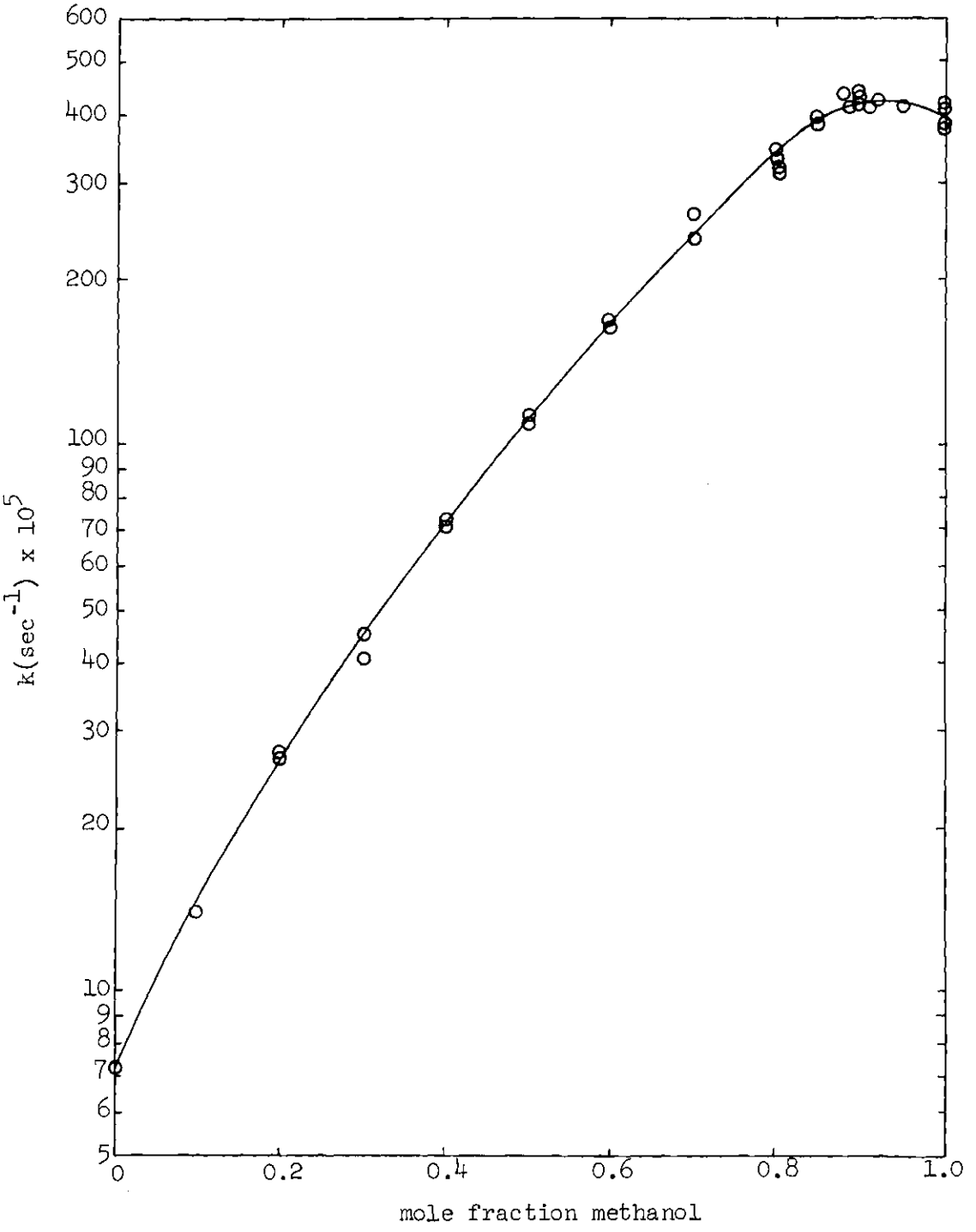

Figure 3. $k_{rac.}$ for $Fe(phen)_3^{2+}$ in Methanol-Water Mixtures at 12.00°C.

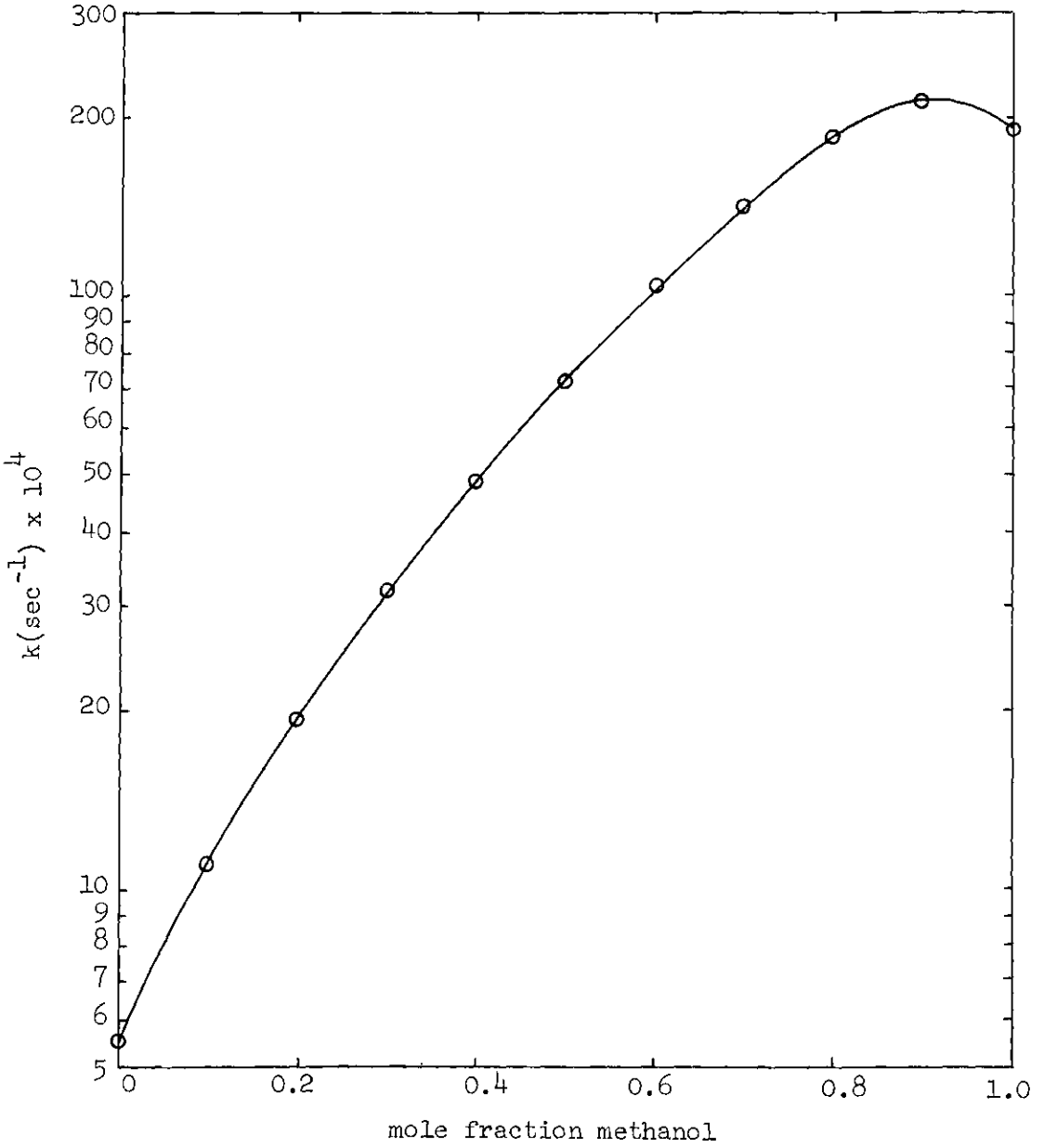

Figure 4. $k_{int.rac.}$ for $Fe(phen)_3^{2+}$ in Methanol-Water Mixtures at 25.00°C.

decreases on addition of nitric acid; and Jensen, Basolo, and Neumann[52] report that the addition of brucine hydrochloride to water increases the racemization rate. Qualitatively, the intramolecular racemization rate curve is similar to the racemization rate data reported by Seiden, Basolo, and Neumann[23] for methanol-water mixtures at 0° C, although their data is not at close enough intervals to show the maximum in rate constant at 0.9 X methanol. The large number of measurements made between 0.8 and 1.0 X methanol, shown in Figure 3, confirms the existance of the maximum. It was felt that the maximum may be due to the onset of extensive ion pairing in solutions of high methanol content and a lower racemization rate constant for the ion pair. Figure 5 shows the dependence of the rate constant on the total perchlorate concentration for added $NaClO_4$ in methanol at 25° C. The data point for no added $NaClO_4$ is from the Arrhenius plot for 1.0 X methanol.

The Arrhenius parameters for racemization rates in methanol-water mixtures were determined by plotting log(k) versus (1/T). Figure 6 shows the variation of E_a, and Figure 7 shows the variation of log(A) with X methanol. The numerical values of E_a and log(A) for these plots are listed in Appendix C. The plot of E_a versus X methanol is linear within the error limits of the data. The plot of log(A) must then be non-linear if the plot of log(k) is to be non-linear. For water the value of E_a of 28.3 Kcal is near that reported by Basolo, et al.[24] of 29 ± 2 Kcal.

Figure 8 shows the variation of the dissociation rate constant with X methanol at 25° C. The rate constant rises and then rapidly decreases as the solvent approaches pure methanol, having a maximum at 0.65 X methanol. The rates are in close agreement with those reported

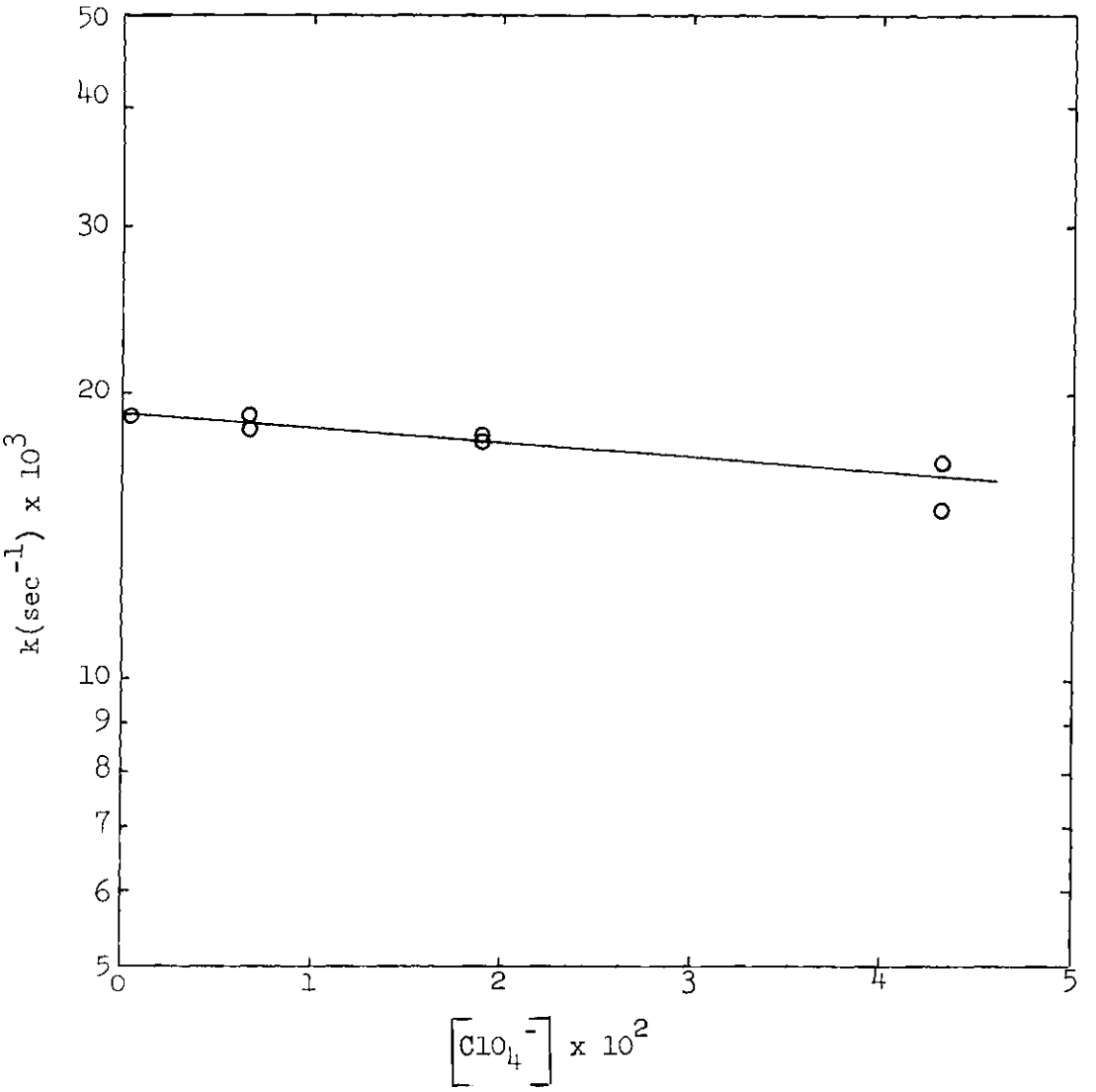

Figure 5. $k_{rac.}$ Versus Total ClO_4^- Concentration in 1.0 X Methanol at 25.00°C.

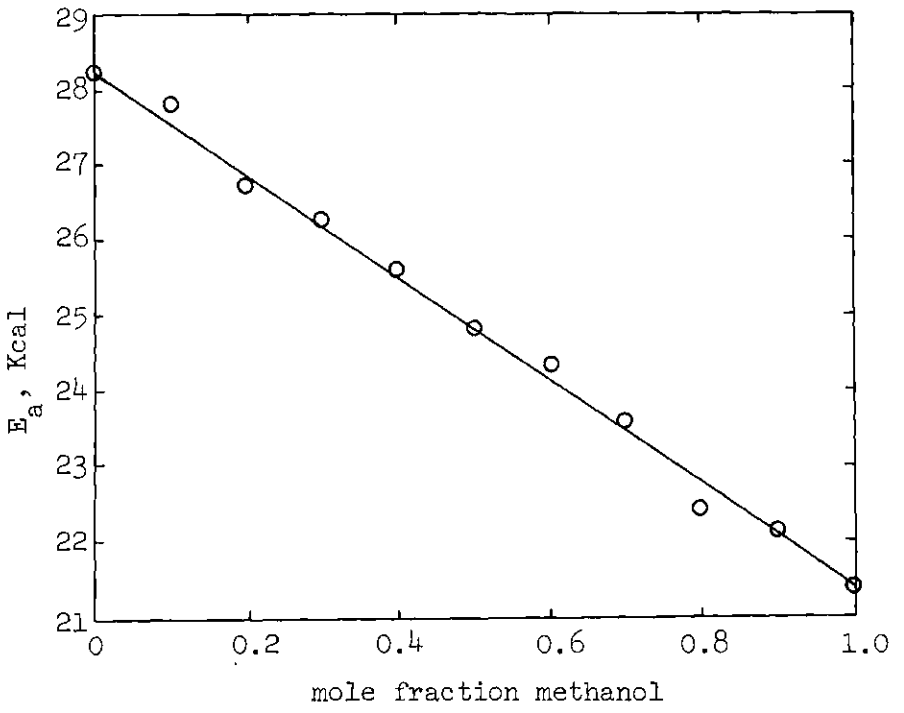

Figure 6. Arrhenius Activation Energy for $k_{rac.}$ of $Fe(phen)_3^{2+}$ in Methanol-Water Mixtures

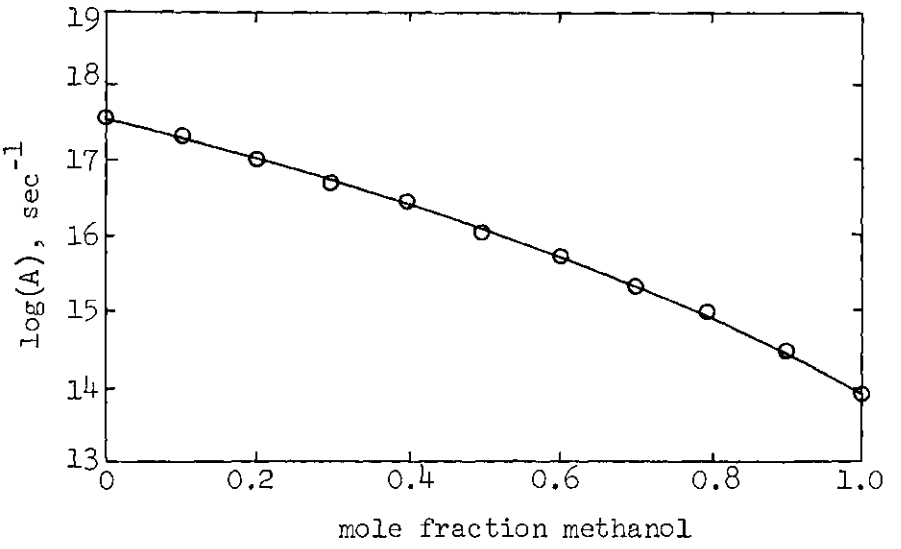

Figure 7. Arrhenius Frequency Factor for $k_{rac.}$ of $Fe(phen)_3^{2+}$ in Methanol-Water Mixtures

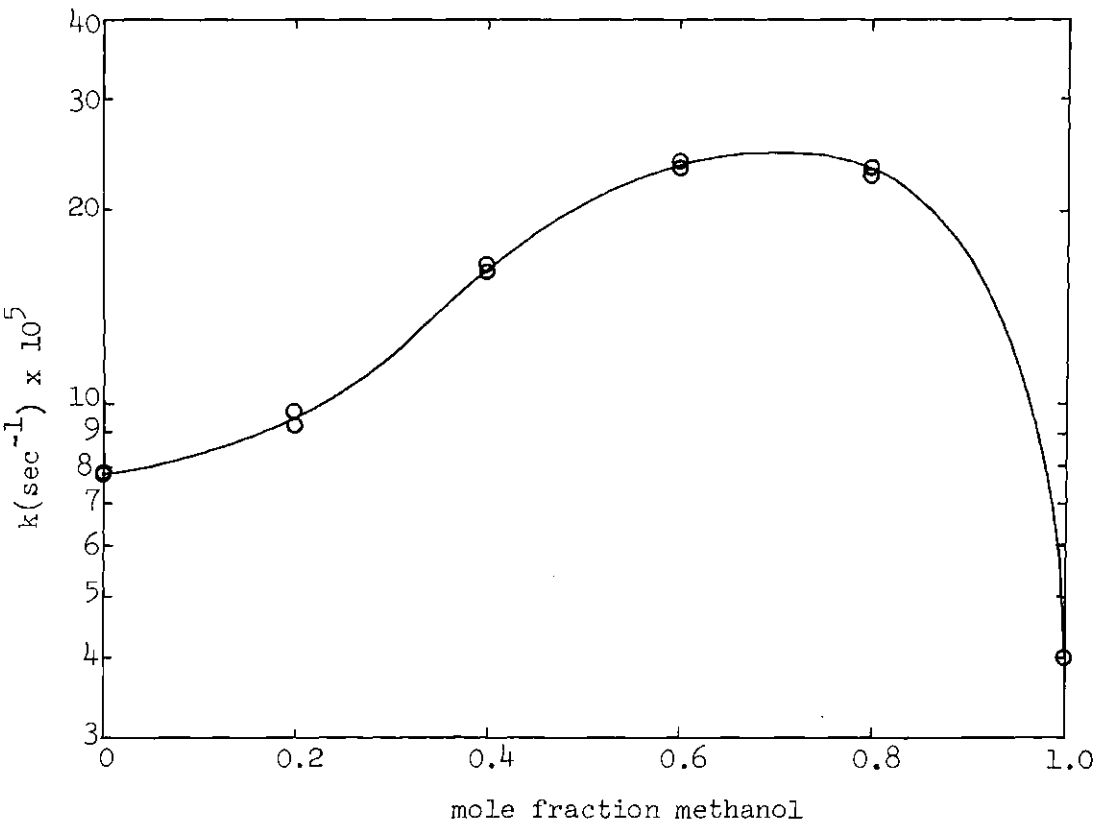

Figure 8. $k_{diss.}$ for $Fe(phen)_3^{2+}$ in Methanol-Water Mixtures at 25.00°C.

by Basolo, et al.[23] at 25.5° C but are slightly larger in the region 0.6-0.8 X methanol.

Acetone-Water Mixtures

Figure 9 shows the variation of the rate constant for intramolecular racemization ($k_{rac.}$-$k_{diss.}$) with X acetone for acetone-water mixtures at 25° C. The racemization rates are extrapolated from Arrhenius plots, and the dissociation rates are interpolated from the plot of k_{diss} versus X acetone (Figure 14). The numerical values of $k_{rac.}$, $k_{diss.}$, and $k_{int.rac.}$ are listed in Appendix D. The data in the region 0.9-1.0 X acetone has a high uncertainty due to the very rapid rates in this region.

Figure 10 shows the variation of the Arrhenius activation energy, and Figure 11 shows the variation of the Arrhenius frequency factor with X acetone for racemization in acetone-water mixtures. Each plot shows a minimum near 0.4 X acetone and a maximum near 0.9 X acetone. The actual existance of the maximum near 0.9 X acetone is not certain. The numerical values of E_a and log(A) are listed in Appendix E.

Figure 12 shows the variation of the rate constant for racemization with the total perchlorate concentration in 1.0 X acetone at 0.3° C. Two distinct curves are observed; one for the dependence on $Fe(phen)_3(ClO_4)_2$ concentration alone, and one for added $NaClO_4$ where the complex concentration is held constant.

Figure 13 shows the rate constants for racemization in 0.800 X acetone versus total perchlorate concentration for added $NaClO_4$ at 11.56° C.

Figure 14 shows the dissociation rate constants in acetone-water mixtures at 25° C.

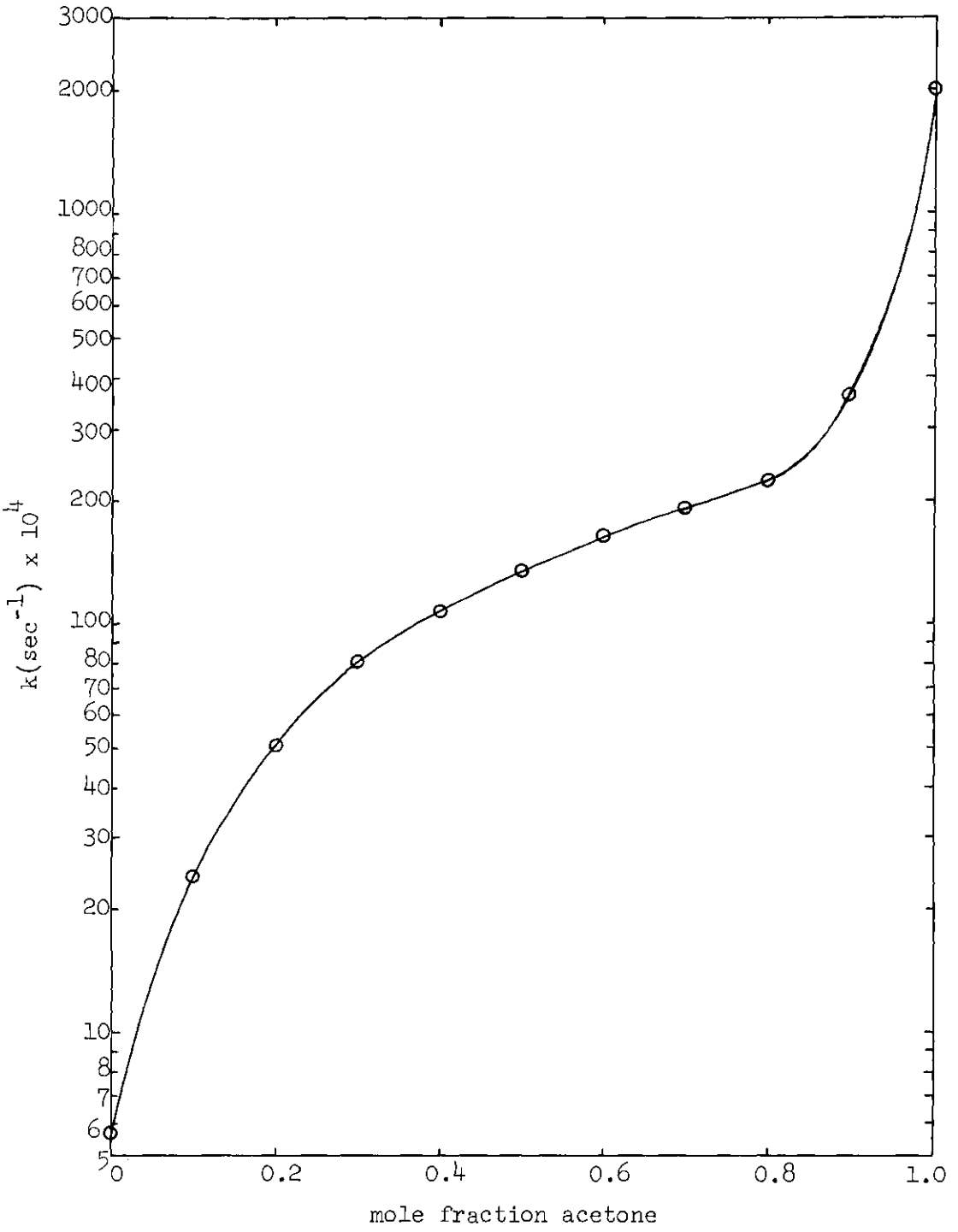

Figure 9. $k_{int.rac.}$ for $Fe(phen)_3^{2+}$ in Aceton-Water Mixtures at 25.00°C.

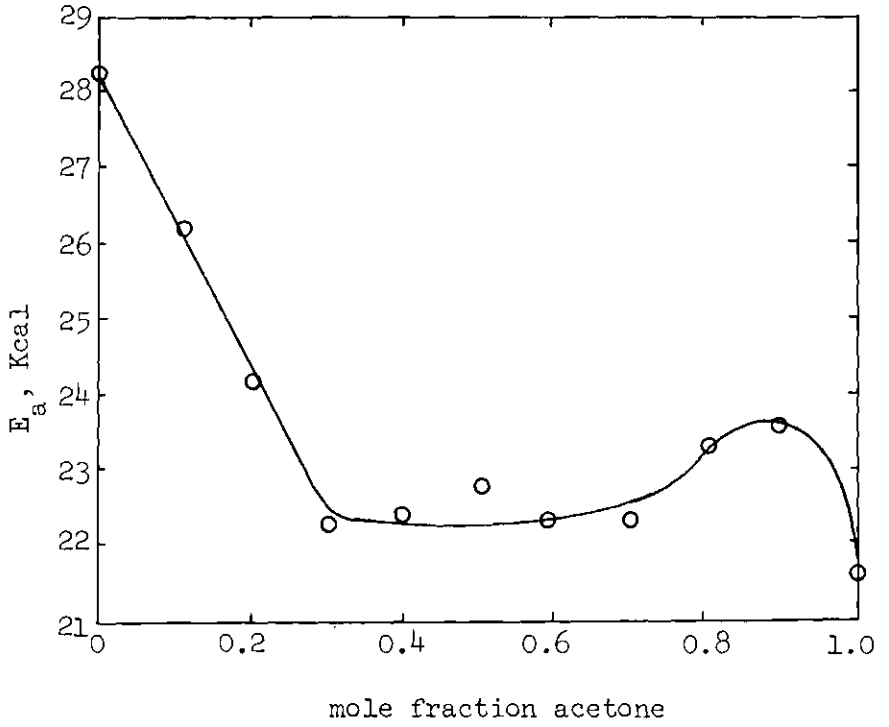

Figure 10. Arrhenius Activation Energy for $k_{rac.}$ of $Fe(phen)_3^{2+}$ in Acetone-Water Mixtures

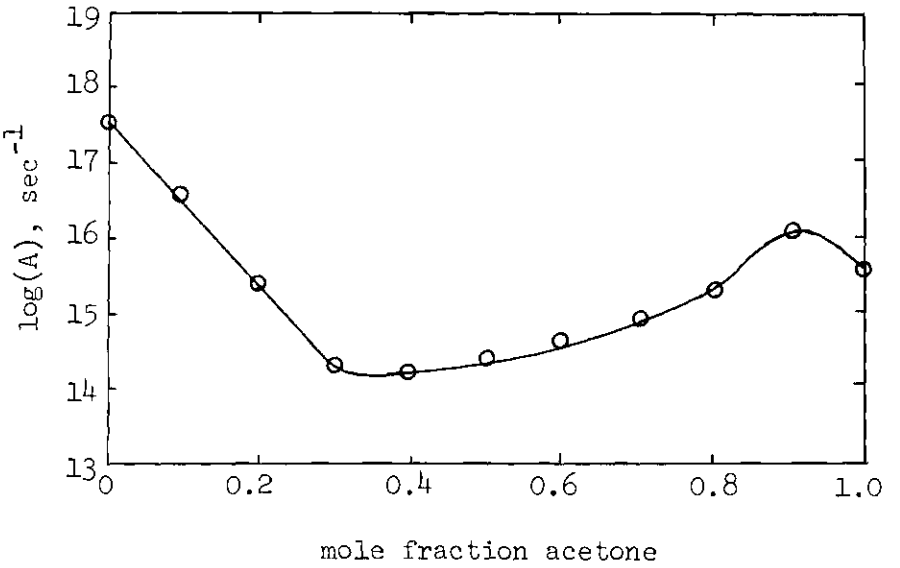

Figure 11. Arrhenius Frequency Factor for $k_{rac.}$ of $Fe(phen)_3^{2+}$ in Acetone-Water Mixtures

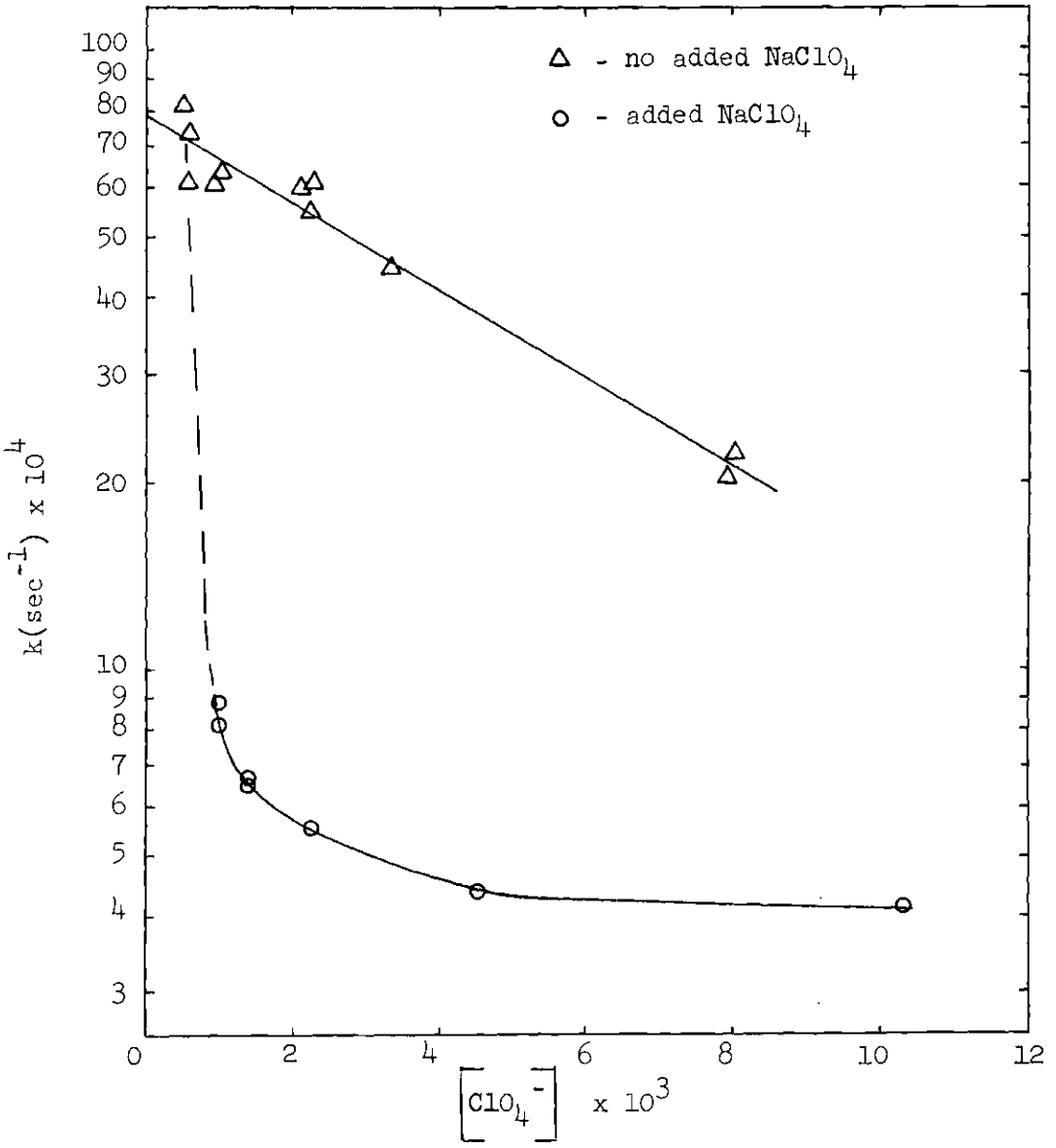

Figure 12. $k_{rac.}$ Versus Total ClO_4^- Concentration in 1.0 X Acetone at 0.3°C.

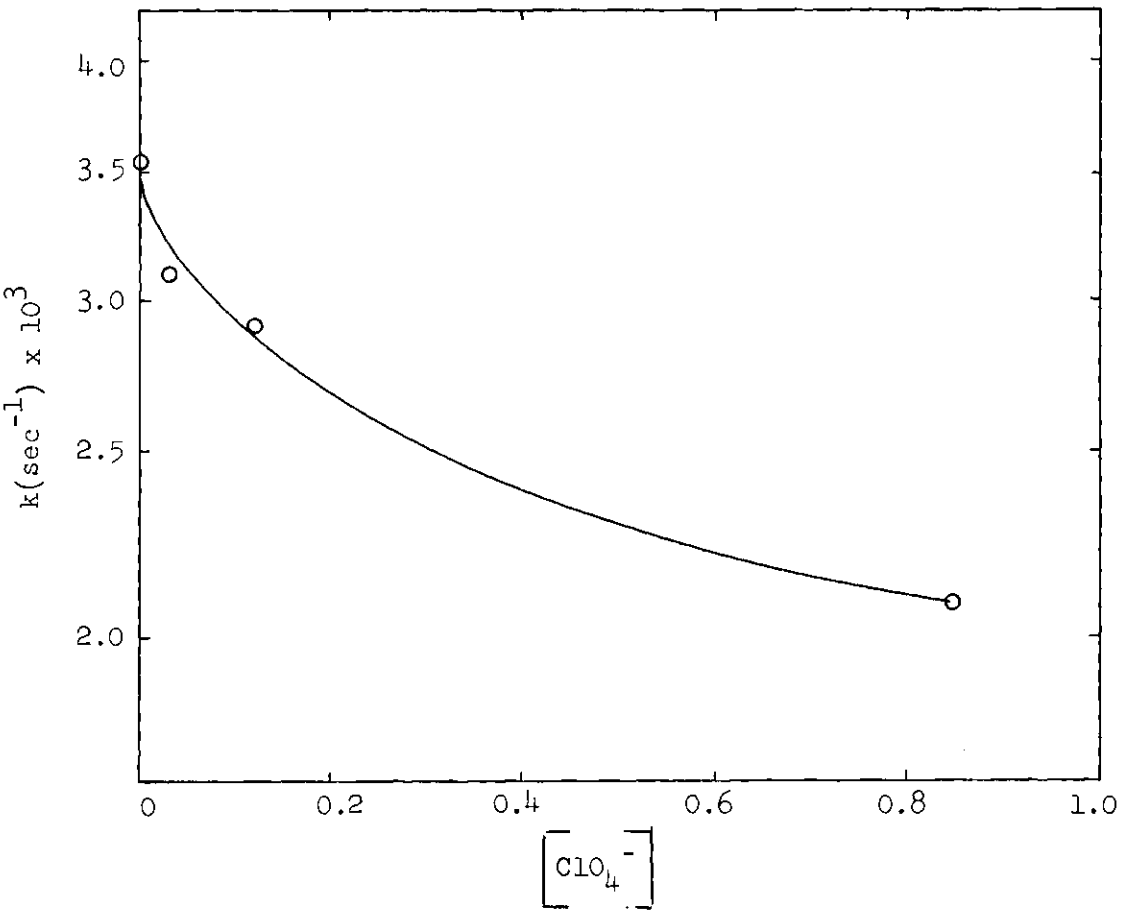

Figure 13. $k_{rac.}$ Versus Total ClO_4^- Concentration in 0.800 X Acetone at 11.56°C.

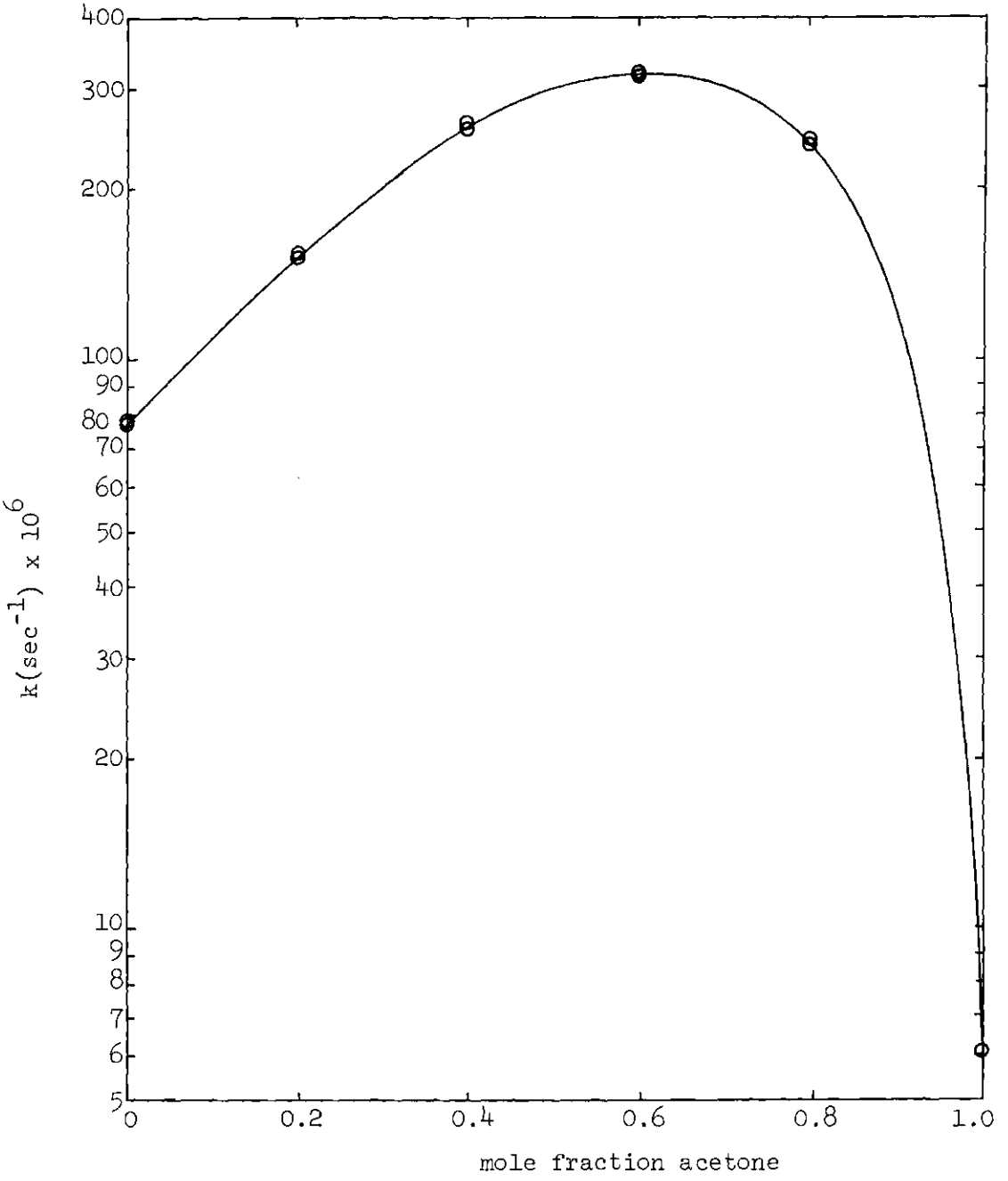

Figure 14. $k_{diss.}$ for $Fe(phen)_3^{2+}$ in Acetone-Water Mixtures at 25.00°C.

N,N-dimethylformamide-Water Mixtures

Figure 15 shows the variation in rate constant for intramolecular racemization with X dimethylformamide for N,N-dimethylformamide-water mixtures at 25° C. The racemization rate constants are extrapolated from Arrhenius plots. The dissociation rates are interpolated from the plot of $k_{diss,}$ versus X dimethylformamide (Figure 19). The numerical values of $k_{rac,}$ $k_{diss,}$ and $k_{int.rac,}$ are listed in Appendix F.

Figure 16 shows the variation of the Arrhenius activation energy, and Figure 17 shows the variation of the Arrhenius frequency factor with X dimethylformamide for the racemization rates. Appendix G lists the numerical values of E_a and log(A) for dimethylformamide-water mixtures.

Figure 18 shows the variation of the rate constant for racemization with the total perchlorate concentration for added $NaClO_4$ in 1.0 X dimethylformamide at 0.3° C.

Figure 19 shows the variation of the rate constant for dissociation with X dimethylformamide at 25° C.

Formamide-Water Mixtures

Figure 20 shows the variation of the rate constant for intramolecular racemization with X formamide for formamide-water mixtures at 25° C. The racemization and dissociation rate constants are interpolated from plots of $k_{rac,}$ and $k_{diss,}$ data at 25° C. Appendix H lists the numerical values of $k_{rac,}$ $k_{diss,}$ and $k_{int.rac}$.

Figure 21 shows the variation of the dissociation rate constant with X formamide at 25° C.

Ethylene Glycol-Water Mixtures

Figure 22 shows the variation of the rate constant for racemization

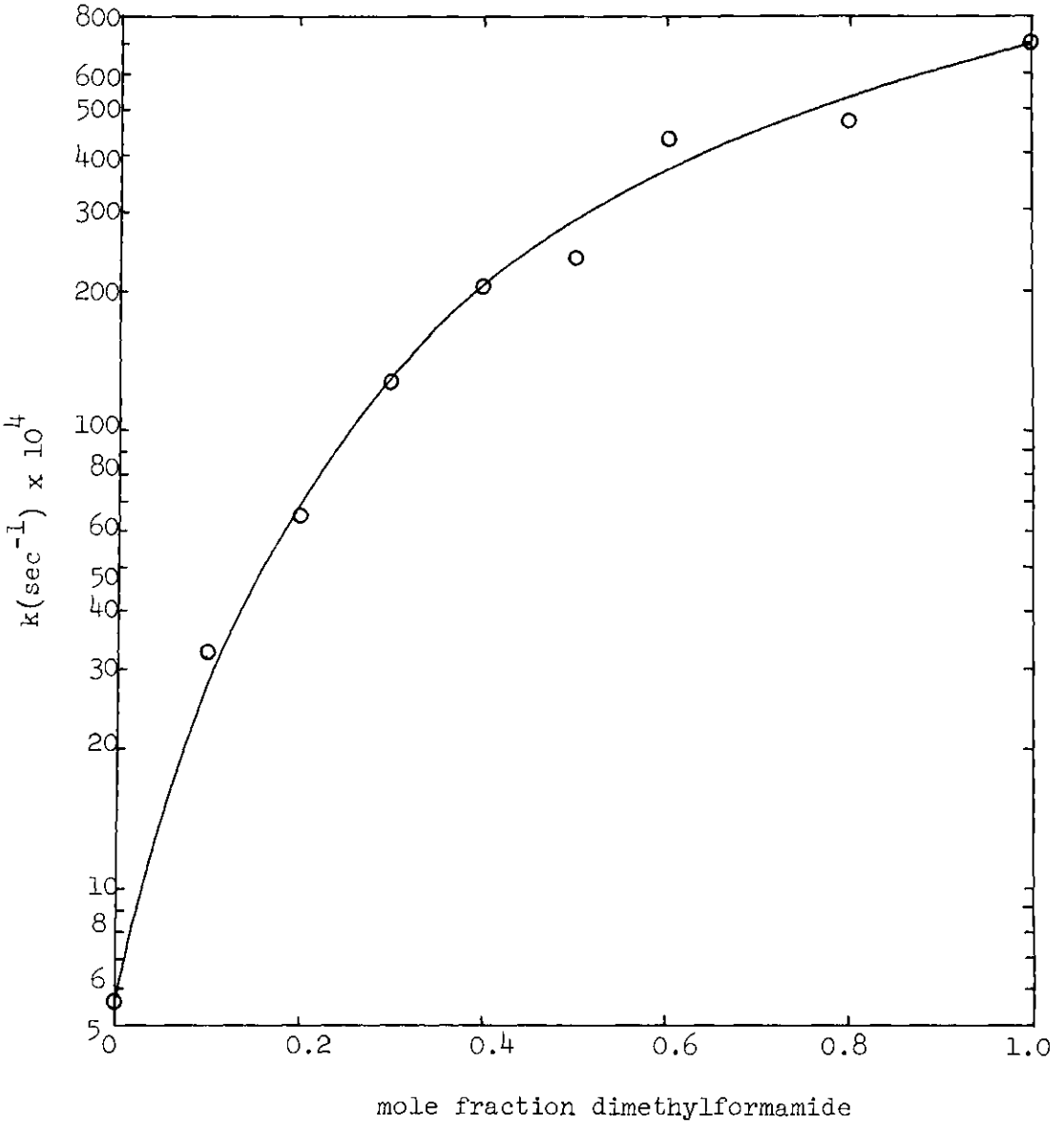

Figure 15. $k_{int.rac.}$ for $Fe(phen)_3^{2+}$ in N,N-dimethylformamide-Water Mixtures at 25.00°C.

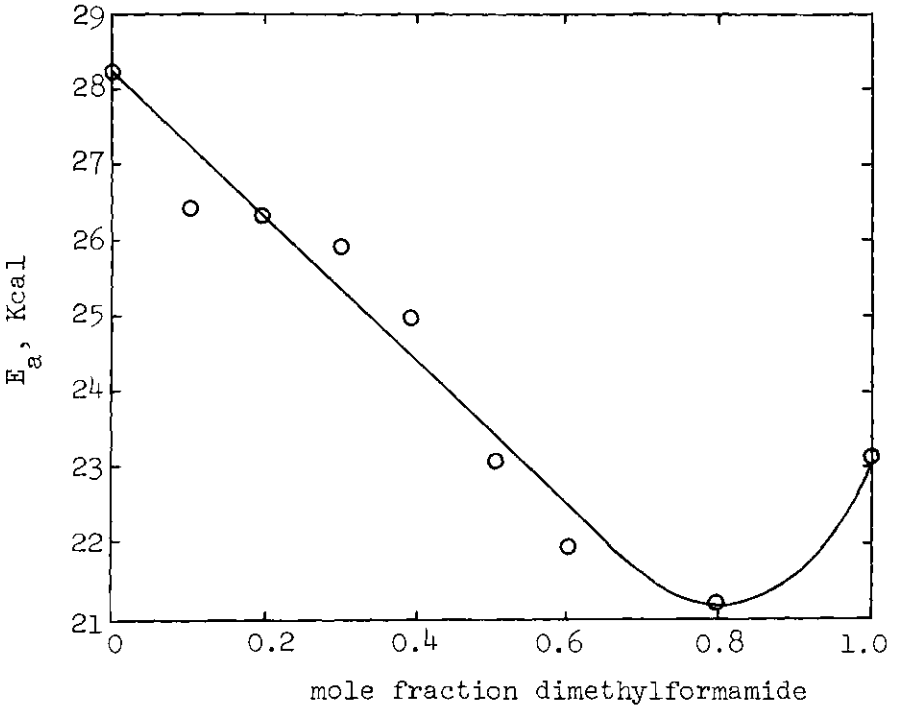

Figure 16. Arrhenius Activation Energy for $k_{rac.}$ of $Fe(phen)_3^{2+}$ in N,N-dimethylformamide-Water Mixtures

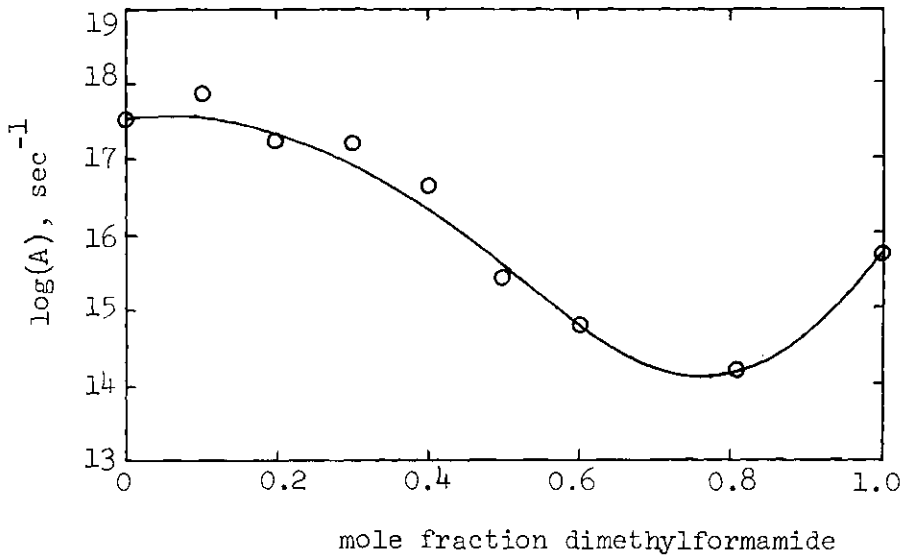

Figure 17. Arrhenius Frequency Factor for $k_{rac.}$ of $Fe(phen)_3^{2+}$ in N,N-dimethylformamide-Water Mixtures

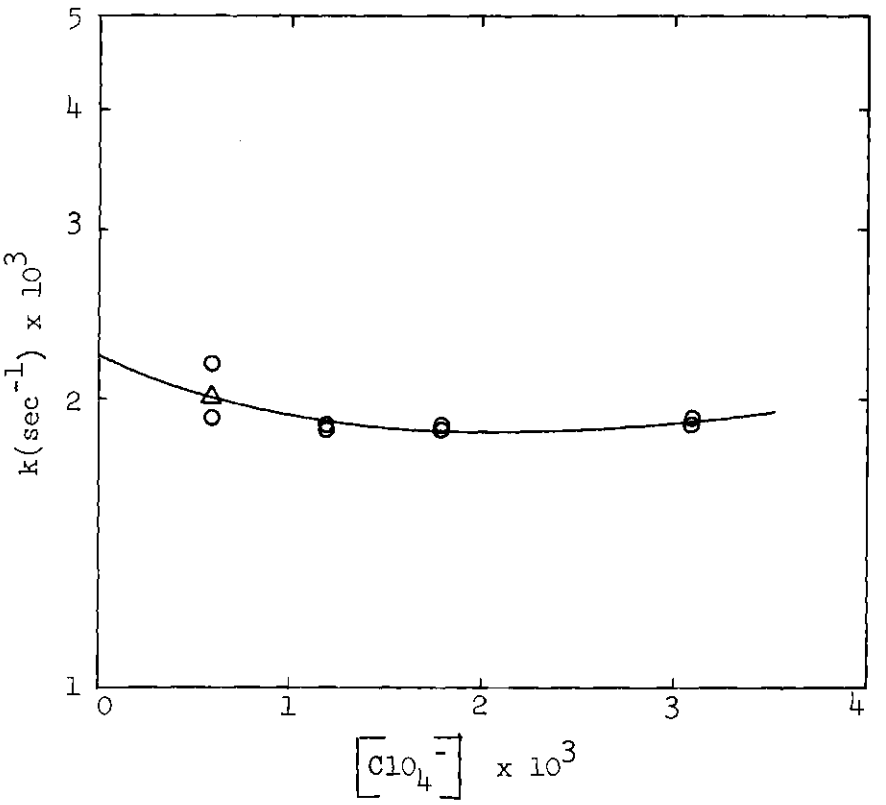

Figure 18. $k_{rac.}$ Versus Total ClO_4^- Concentration in 1.0 X N,N-dimethylformamide at 0.30°C.

○ - single experimental data points

△ - Arrhenius interpolation in 1.0 X dimethylformamide

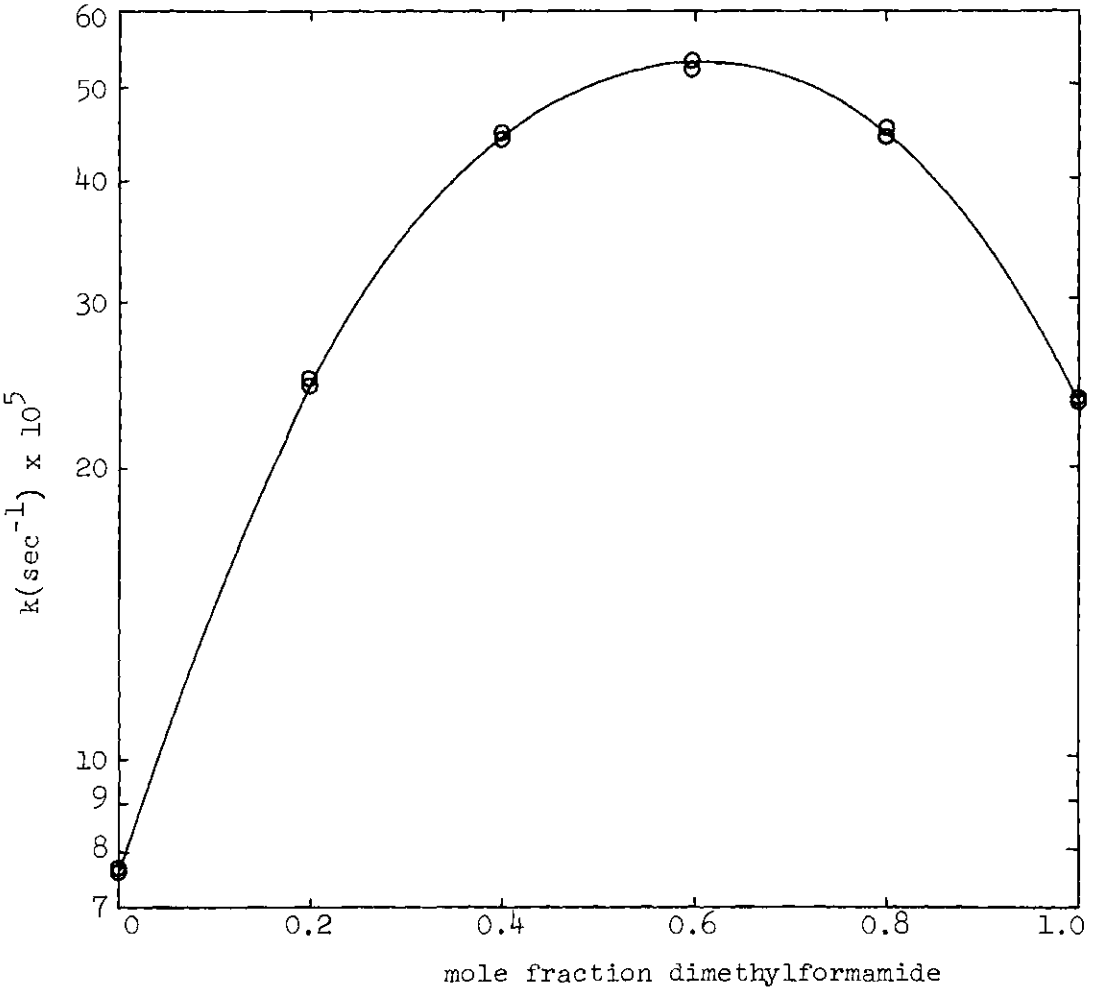

Figure 19. $k_{diss.}$ for $Fe(phen)_3^{2+}$ in N,N-dimethylformamide-Water Mixtures at 25.00°C.

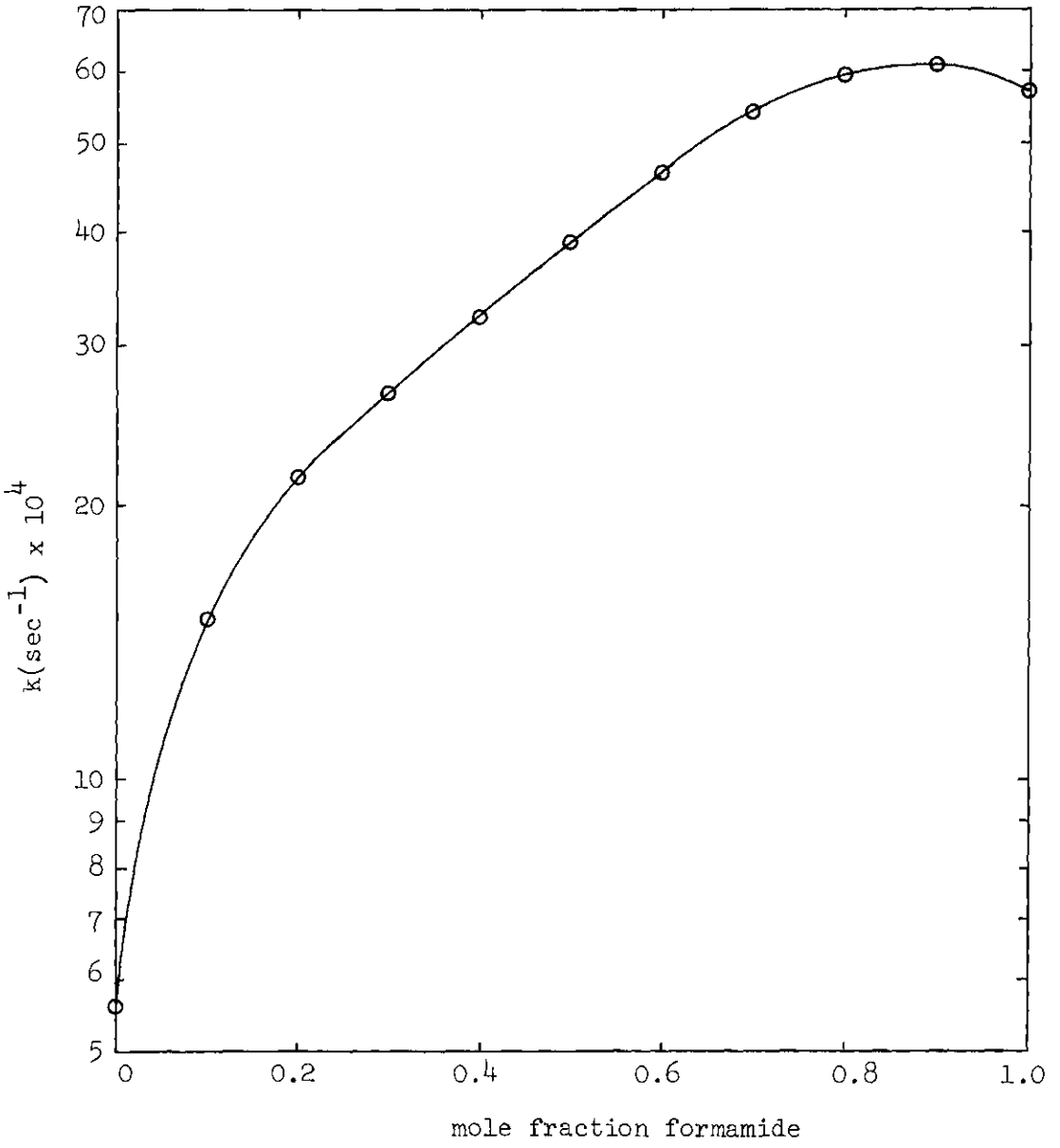

Figure 20. $k_{int.rac.}$ for $Fe(phen)_3^{2+}$ in Formamide-Water Mixtures at 25.00°C.

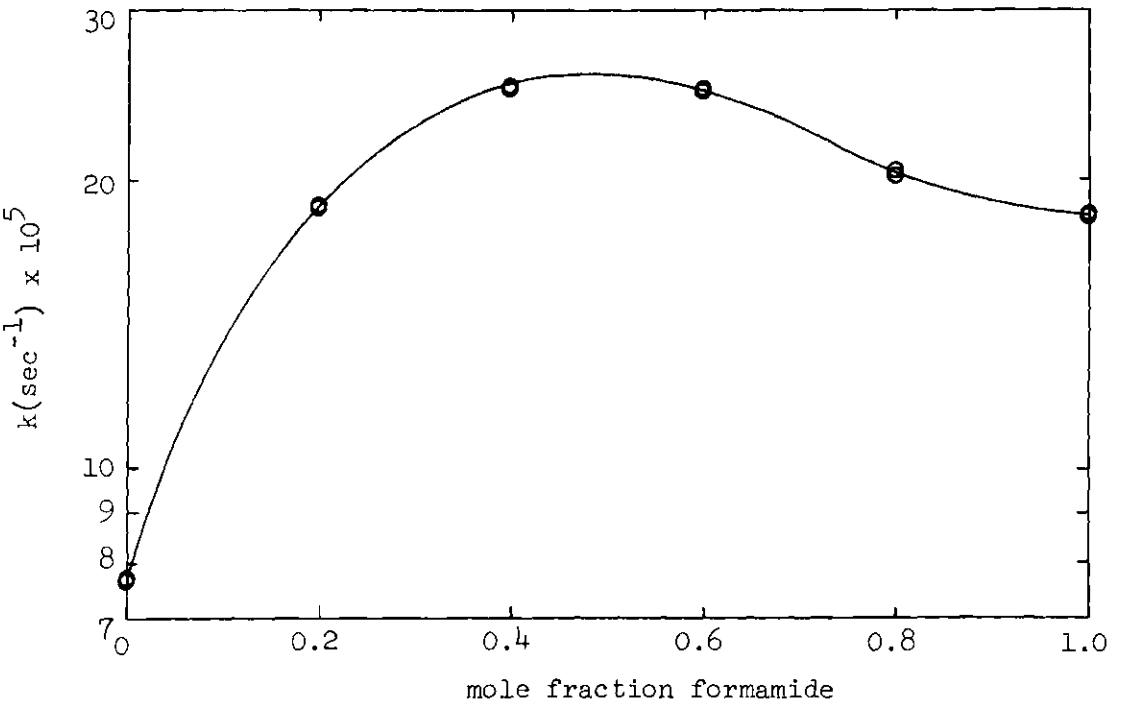

Figure 21. $k_{diss.}$ for $Fe(phen)_3^{2+}$ in Formamide-Water Mixtures at 25.00°C.

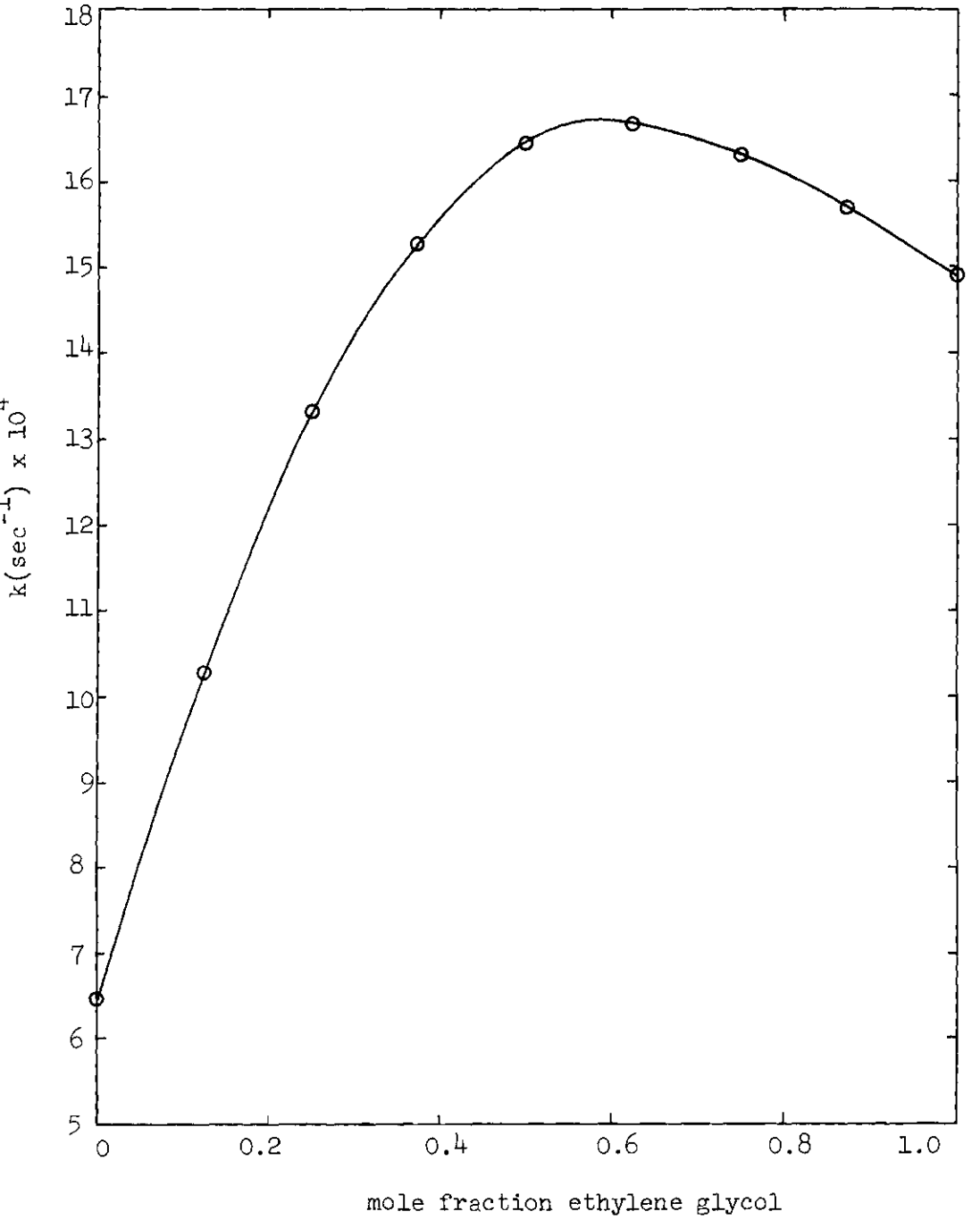

Figure 22. $k_{rac.}$ for $Fe(phen)_3^{2+}$ in Ethylene Glycol-Water Mixtures at 25.00°C.

with X ethylene glycol for ethylene glycol-water mixtures at 25° C. Appendix I lists the numerical values of k_{rac}.

Figure 23 shows the variation of the Arrhenius activation energy, and Figure 24 shows the variation of the Arrhenius frequency factor for racemization in ethylene glycol-water mixtures. Appendix J lists the numerical values of E_a and log(A) for this system.

Glycerol-Water Mixtures

Figure 25 shows the variation of the rate constant for racemization versus X glycerol for glycerol-water mixtures at 25° C. Appendix K lists the numerical values of k_{rac}.

The Arrhenius activation energy for racemization in 0.100 X glycerol is 28.0 Kcal, and in 0.835 X glycerol it is 33.5 Kcal. The logarithms of the frequency factors are: $\log(A) = 17.3_5$ for 0.100 X glycerol, and log(A) = 20.6 for 0.835 X glycerol.

Acetonitrile

The average rate constant for racemization in acetonitrile at 25° C is 1.48×10^{-2} sec.$^{-1}$. Figure 26 shows the rate constants for racemization at 25° C versus total perchlorate concentration for added $NaClO_4$. The dissociation rate constant at 25° C is 2.03×10^{-6}.

Acetic Acid

The average rate constant for racemization in acetic acid at 25° C is 3.71×10^{-3} sec.$^{-1}$, and for dissociation it is 7.6×10^{-7} sec.$^{-1}$.

Ethylene Carbonate-Water Mixtures

The rate constant for racemization in 0.100 X ethylene carbonate at 24.42° C is 1.90×10^{-3} sec.$^{-1}$.

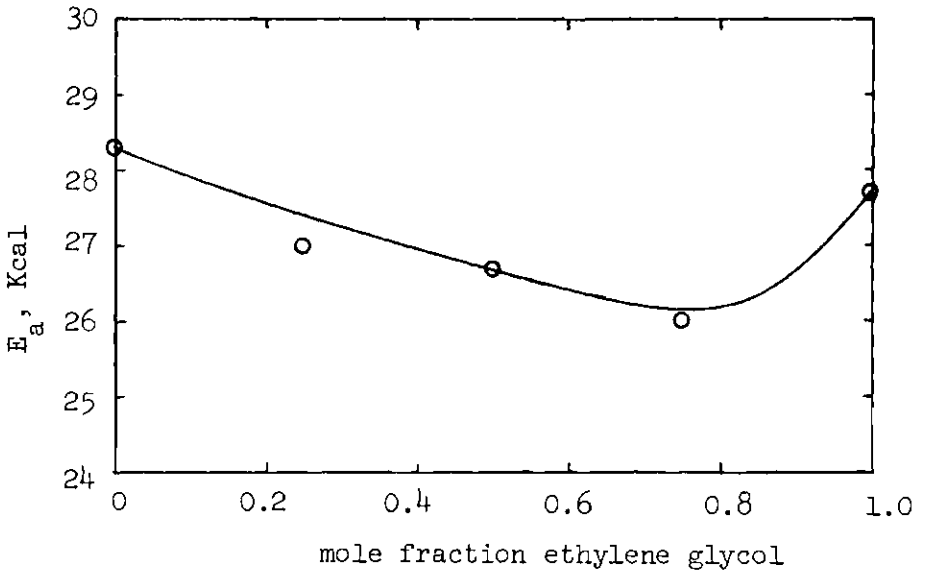

Figure 23. Arrhenius Activation Energy for $k_{rac.}$ of $Fe(phen)_3^{2+}$ in Ethylene Glycol-Water Mixtures

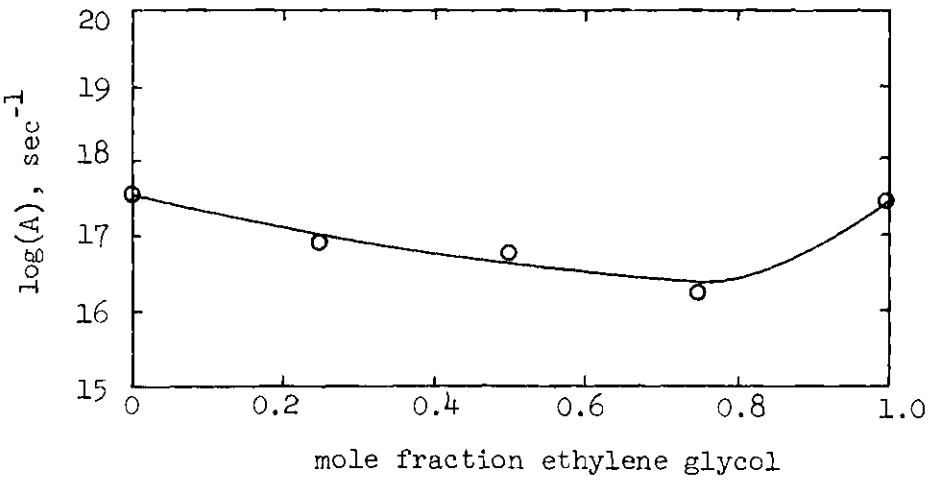

Figure 24. Arrhenius Frequency Factor for $k_{rac.}$ of $Fe(phen)_3^{2+}$ in Ethylene Glycol-Water Mixtures

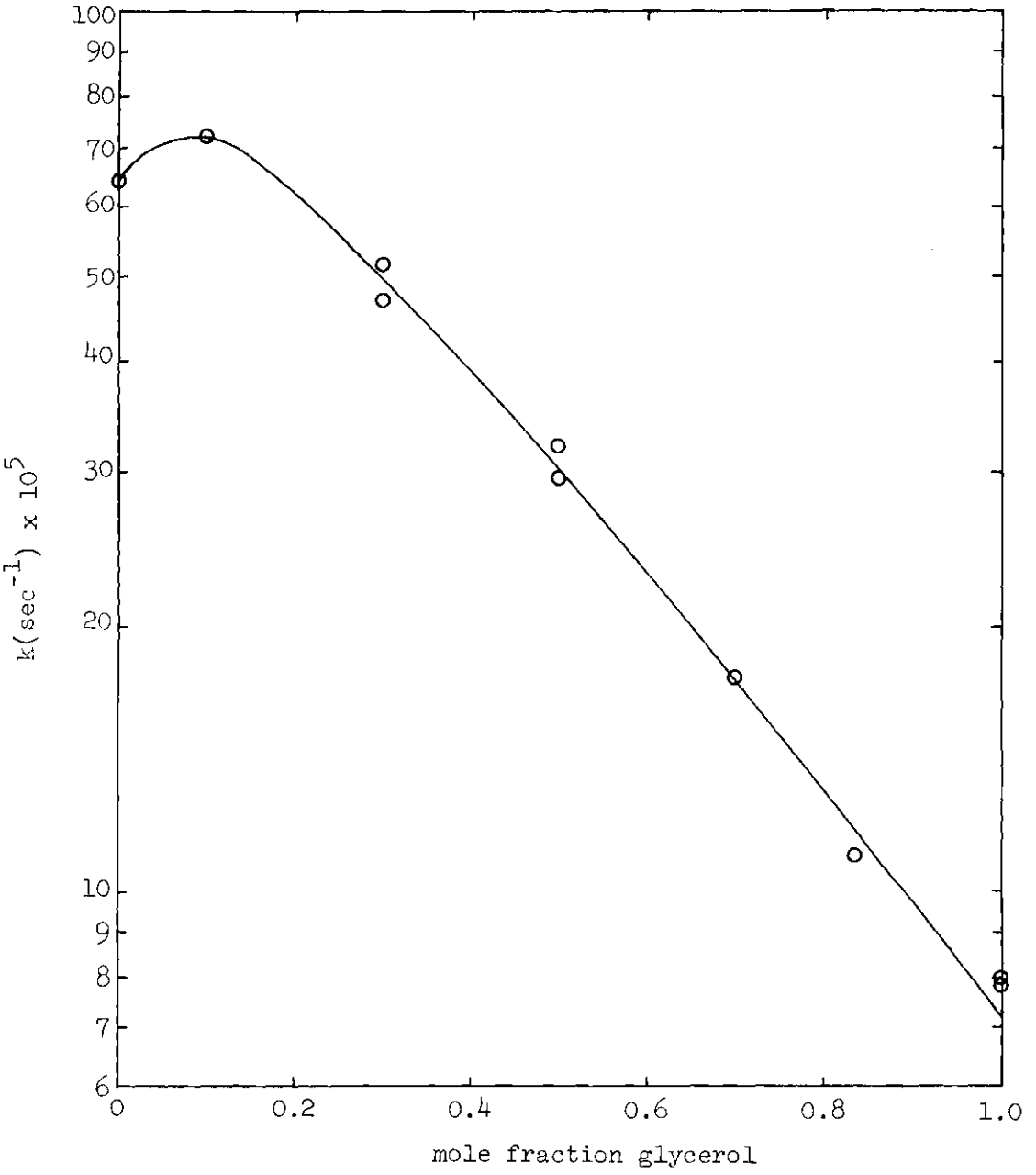

Figure 25. $k_{rac.}$ for $Fe(phen)_3^{2+}$ in Glycerol-Water Mixtures at 25.00°C.

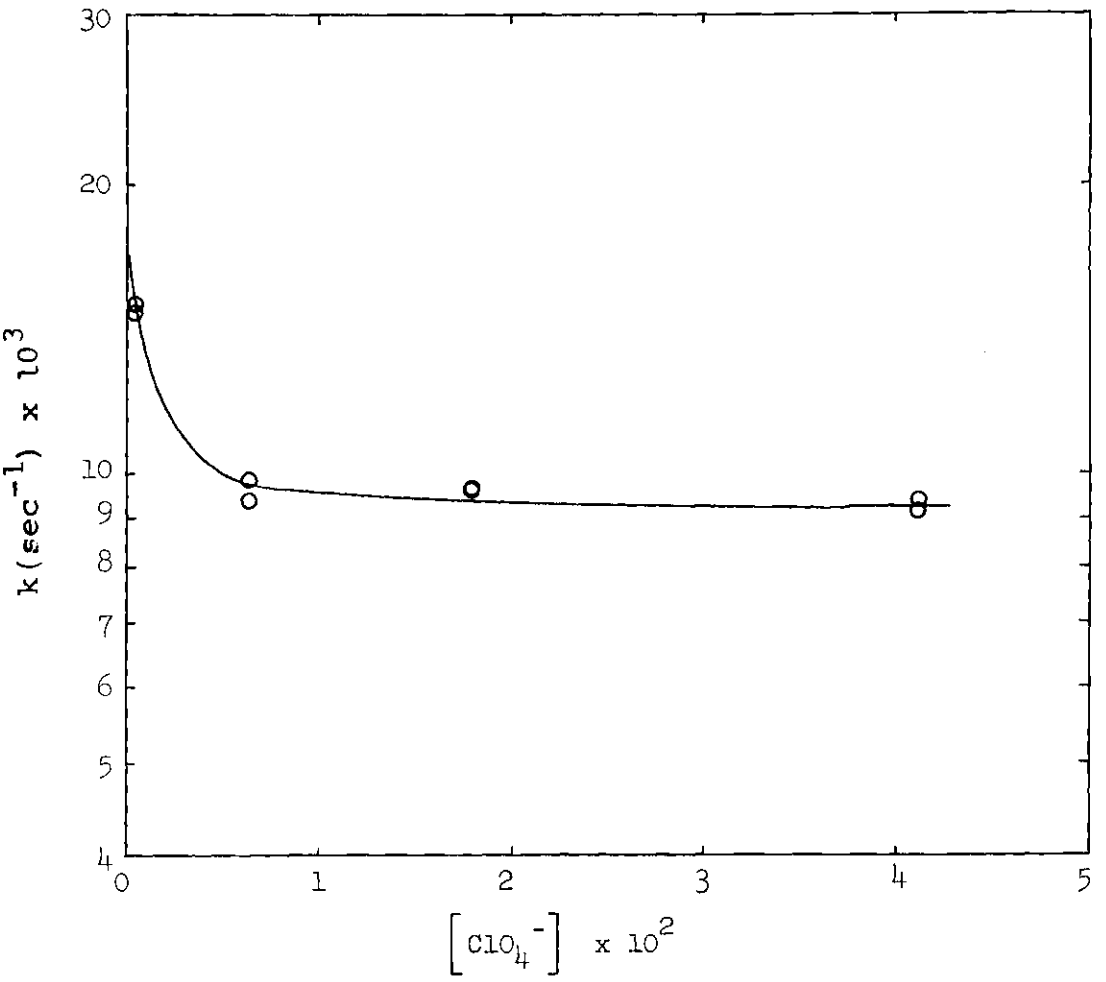

Figure 26. $k_{rac.}$ Versus Total ClO_4^- Concentration in 1.0 X Acetonitrile at 25.00°C.

Urea-Water Mixtures

The rate constant for racemization in 0.100 X urea at 24.42° C is 9.42×10^{-4} sec.$^{-1}$.

Solubilities

$Fe(phen)_3(ClO_4)_2$

The weight loss on heating and the Karl Fischer moisture determinations on $Fe(phen)_3(ClO_4)_2$ give, respectively, 0.09 and 0.37 moles of H_2O per mole of $Fe(phen)_3(ClO_4)_2$. Thus, this salt is best formulated as an anhydrous salt and not as the dihydrate as suggested by Pfeiffer and Werdelmann[43]. The water which was found probably came from inclusions in the crystals or was absorbed on the surface of the crystals. Heating under vacuum might not break open all of the inclusions but would remove the water absorbed on the surface. The Karl Fischer titration would indicate both the surface water and that which was trapped in inclusions. The infrared spectra on crystals of $Fe(phen)_3(ClO_4)_2$ grown in other solvents do not show significant bands due to the solvent. It is concluded, therefore, that the solid in equilibrium with the saturated solutions in the solubility studies is best described as containing no solvent of crystallization. It should be remembered that the solid used in the solubility studies was thoroughly dried while the solid used in the moisture determinations was not dried under nearly as drastic conditions in order to prevent loss of possible crystal water prior to the moisture determinations.

The solubilities of $Fe(phen)_3(ClO_4)_2$ in water, acetone, acetonitrile, formamide, N,N-dimethylformamide, methanol, dimethylsulfoxide,

glycerol, ethylene glycol, and acetic acid are listed in Table 4. No literature data on the solubility of this compound is available for comparison. The solubility in acetic acid varied from measurement to measurement in a random way. The measured values differed by as much as a factor of five. No reason for this is known, although the presence of small amounts of water in the acetic acid increased the solubility sharply. The value given is felt to be near the true value, but the error may be much larger than for the other solvents. The solubilities of $Fe(phen)_3(ClO_4)_2$ in mixtures of water with acetone, methanol, and N,N-dimethylformamide are listed in Table 5. The solubilities versus solvent composition for mixed solvents are shown in Figures 27 and 28. There are pronounced maxima in the solubilities in acetone-water and methanol-water mixtures. There is a probable maximum near 0.9 X dimethylformamide in the dimethylformamide-water mixtures.

Naphthalene

The solubilities of naphthalene in water, acetone, acetonitrile, formamide, N,N-dimethylformamide, methanol, dimethylsulfoxide, glycerol, ethylene glycol, and acetic acid are listed in Table 8. The values determined here agree well with published values[54].

Solvent	This work	Literature[54]
water	0.0300	0.030 g/l
acetone	363	352
methanol	74.3	73.1
acetic acid	113	128

The literature values for acetone and acetic acid are interpola-

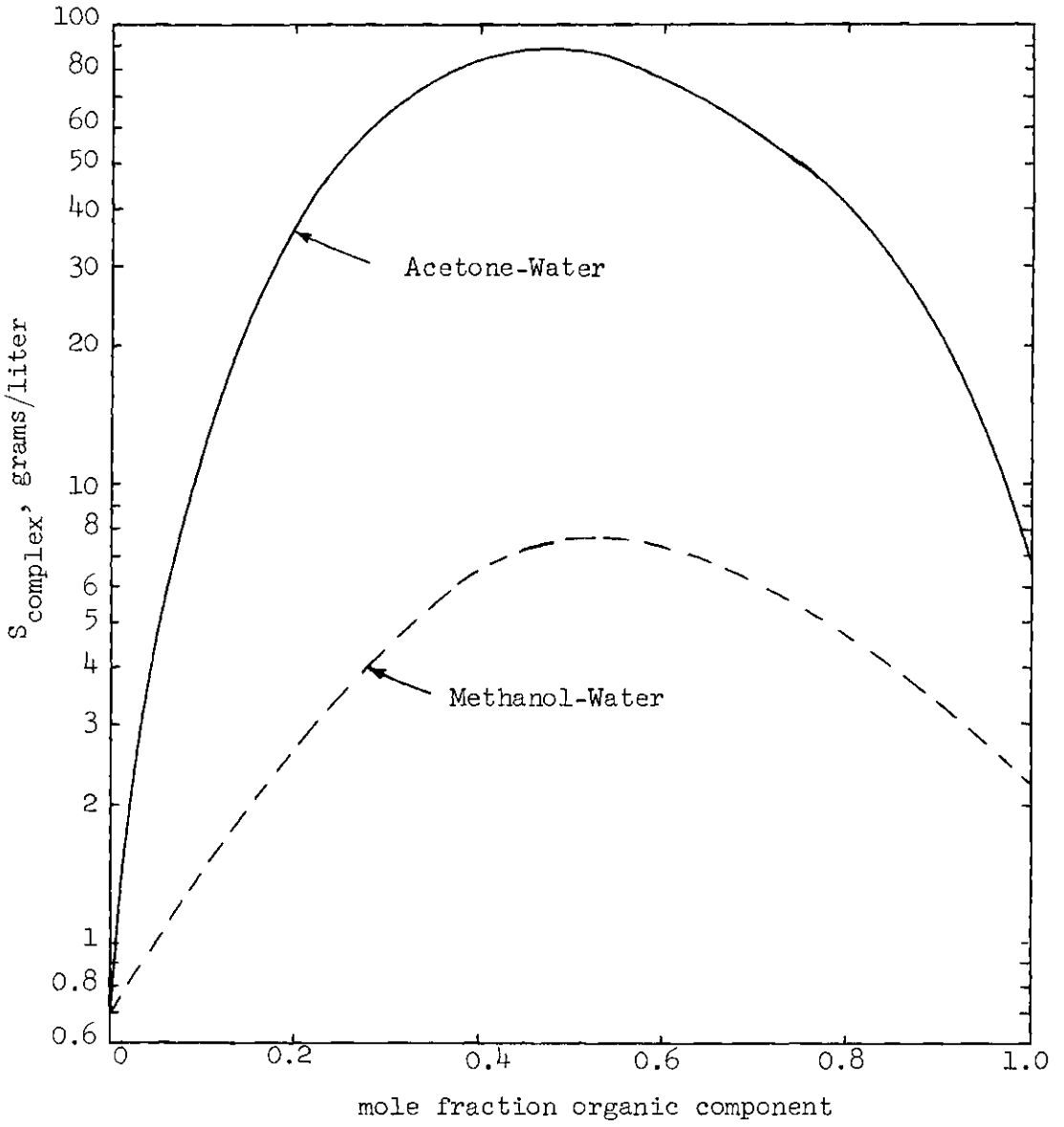

Figure 27. Solubility of $Fe(phen)_3(ClO_4)_2$ in Acetone-Water and Methanol-Water Mixtures at 25.00°C.

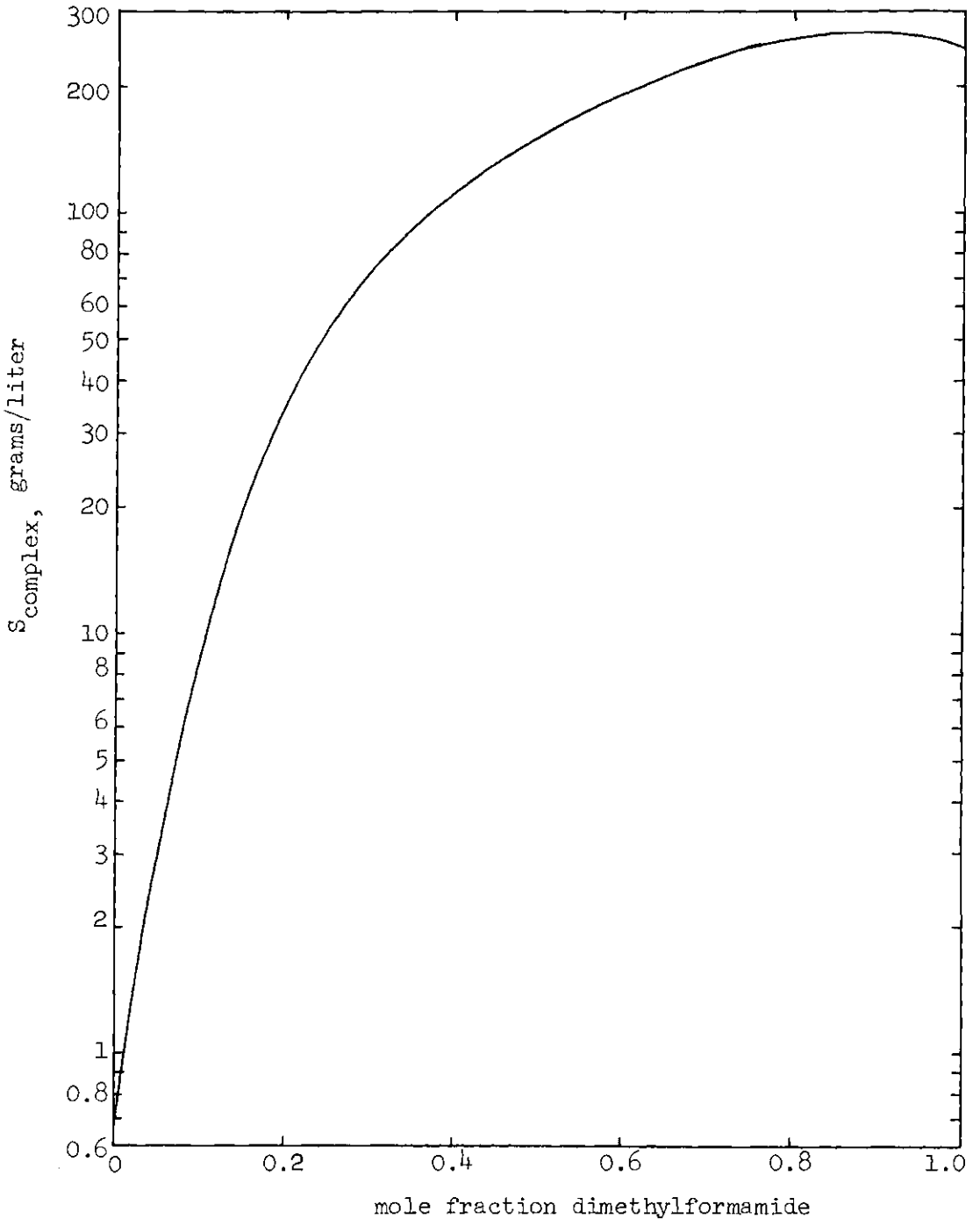

Figure 28. Solubility of $Fe(phen)_3(ClO_4)_2$ in N,N-dimethylformamide-Water Mixtures at 25.00°C.

tions of percent solubilities at various temperatures and use our values of the solution density to convert from weight percent to grams per liter.

The solubilities in mixtures of water with acetone, methanol, and dimethylformamide are shown in Figure 29 and listed in Table 9.

NMR Measurements

The chemical shifts of the 5,6 protons of the phenanthroline ligands in $Fe(phen)_3(ClO_4)_2$ relative to external benzene are listed in Tables 10 and 11. Solvent systems are: water, acetone, N,N-dimethylformamide, dimethylsulfoxide, acetonitrile, and methanol. Table 11 also lists the chemical shifts in mixtures of water with acetone and dimethylformamide. Figure 30 shows the variation in chemical shift with solvent composition for the mixed solvents. Table 12 and Figure 31 show the variation of chemical shift with total perchlorate concentration in acetone.

Oxidation of $Fe(phen)_3^{2+}$ in Acetic Acid

In acetic acid solution, $Fe(phen)_3^{2+}$ is oxidized by nitrogen(IV) and nitrogen(V) species in the presence of $Ni(H_2O)_6(ClO_4)_2$, H_2SO_4, $HClO_4$, $Mg(ClO_4)_2$, and HPO_3. The product of the reaction is identified as $Fe(phen)_3^{3+}$. In water or acetic acid-water mixtures, the reaction is reversed and $Fe(phen)_3^{3+}$ is reduced to $Fe(phen)_3^{2+}$. Nitrogen(II) species in acetic acid reduce the Fe(III) complex to the Fe(II) complex. No induction period prior to oxidation is observed with nitrogen dioxide. An induction period is observed with nitrogen(V) species which increases in the order: HNO_3 > ferric nitrate > nickel(II) nitrate, cobalt(II) nitrate, > magnesium nitrate, sodium nitrate, and potassium nitrate.

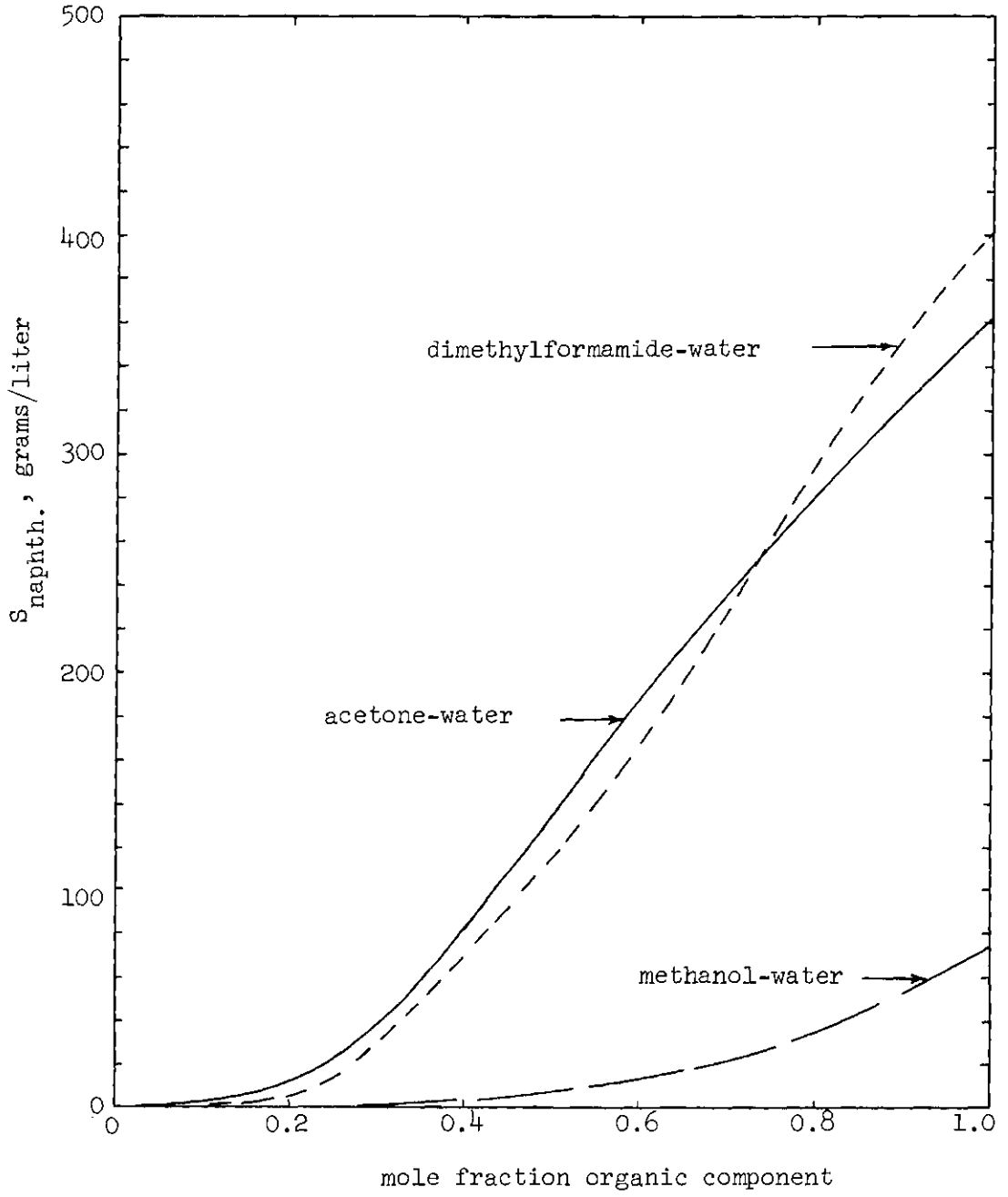

Figure 29. Solubility of Naphthalene in Mixed Solvents at 25.00°C.

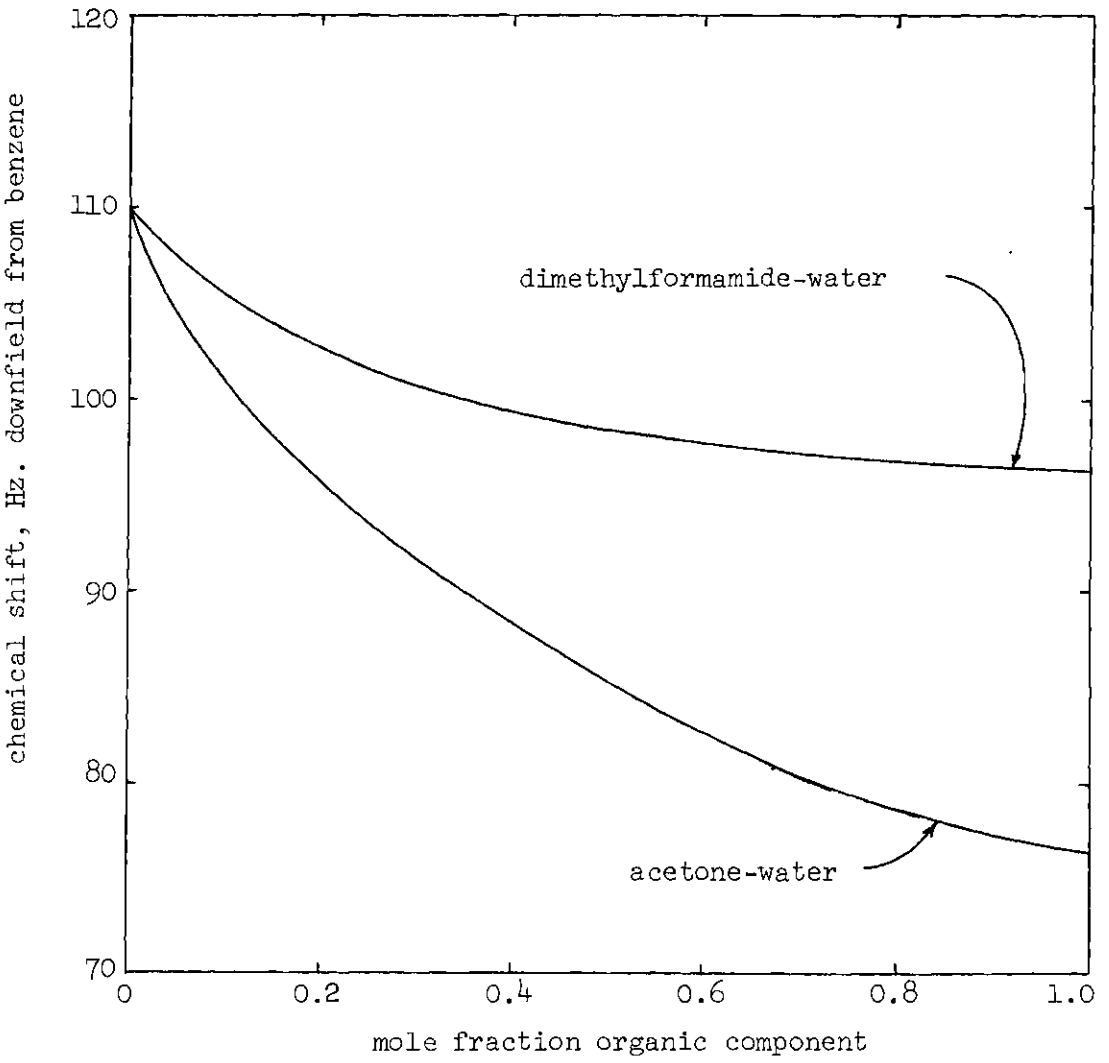

Figure 30. Chemical Shifts of 5,6 Protons in $Fe(phen)_3^{\cdot}(ClO_4)_2$ in Acetone-Water and N,N-dimethylformamide-Water Mixtures

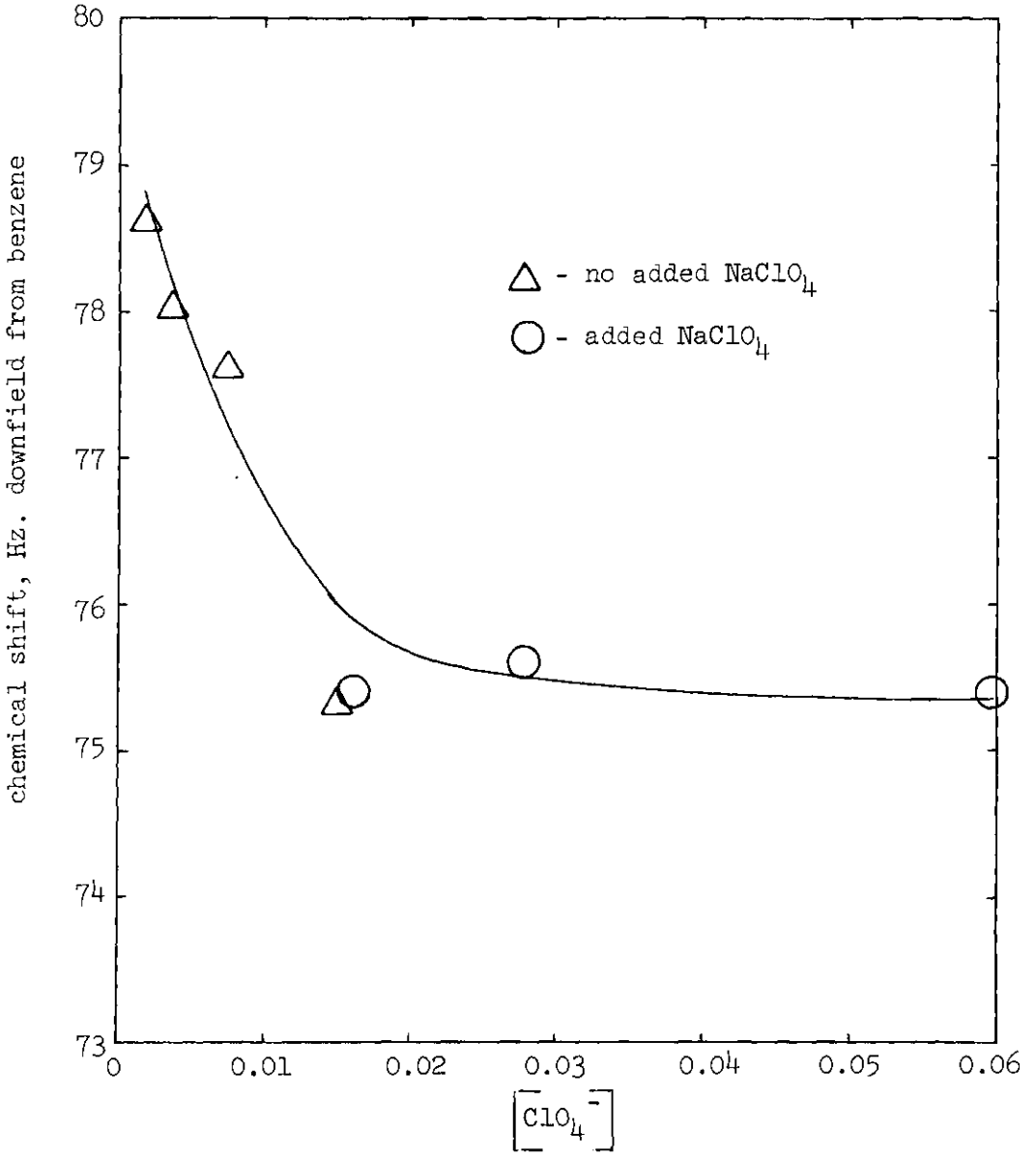

Figure 31. Chemical Shifts of the 5,6 Protons in $Fe(phen)_3(ClO_4)_2$ Versus Total ClO_4^- Concentration in Acetone

CHAPTER IV

DISCUSSION OF RESULTS

Racemization Rates

In water at 25° C racemization occurs by an intramolecular process 87.9 percent of the time, the remainder occurring by dissociation. In methanol, acetone, formamide, N,N-dimethylformamide, acetonitrile, and acetic acid, the intramolecular process increases in importance over the dissociative process relative to water. Figure 32 shows the function $(k_{rac.}-k_{diss.})/k_{diss.}$ for mixtures of water with methanol, acetone, formamide, and dimethylformamide. This function is the ratio of racemizations occurring by intramolecular processes to those occurring by dissociative processes. It shows the predominance of intramolecular racemization on going from aqueous to organic media in a dramatic way.

Seiden, Basolo, and Neumann[23] have suggested that in methanol-water mixtures, the racemization rates might be dependent on increased freedom of movement of the ligands as methanol replaces water in the solvation sphere of the $Fe(phen)_3^{2+}$ ion. For methanol-water mixtures at 25° C, the racemization rate constant, activation energy, solvent viscosity, and solvent volume shrinkage on mixing are shown versus solvent composition in Figure 33. The volume shrinkage has a maximum near 0.4 X methanol, and the viscosity has a maximum near 0.25 X methanol. Nothing about the behavior of the rate constant or the activation energy suggests that either is related to the volume shrinkage or the viscosity.

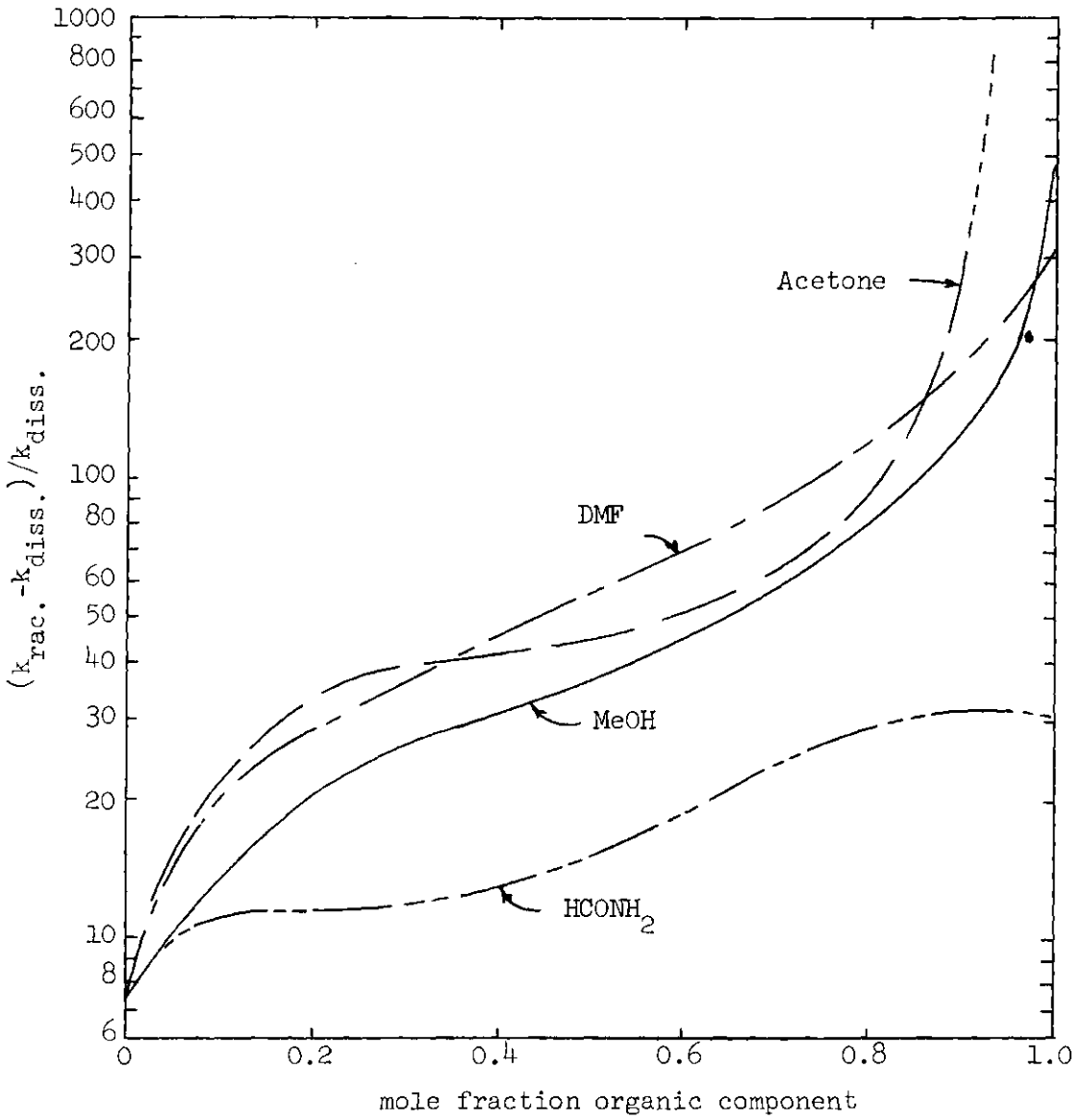

Figure 32. Ratio of Intramolecular Racemization to Racemization by Dissociation at 25°C. in Various Solvents

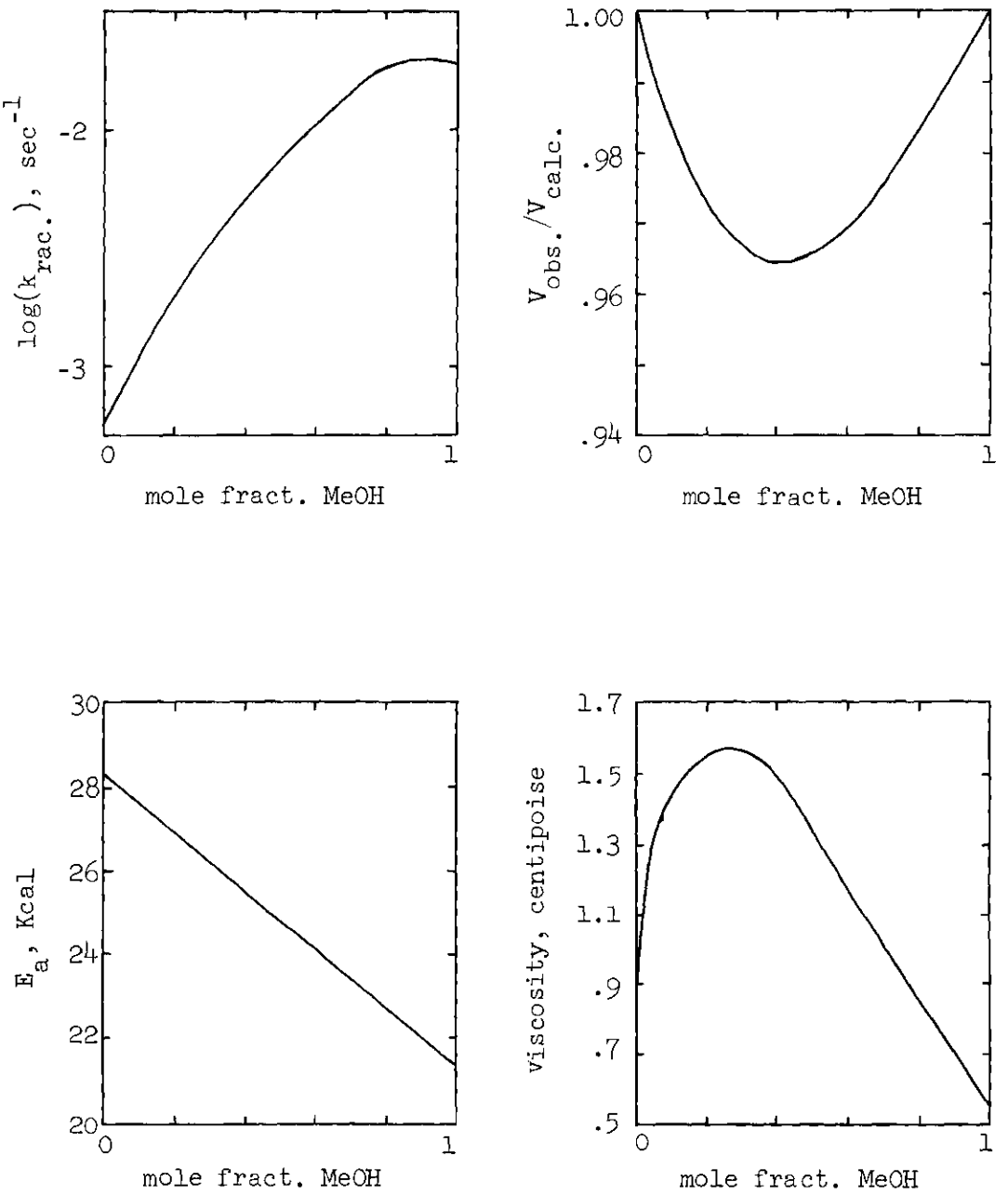

Figure 33. Log(k), E_a, Viscosity, and Volume Defect on Mixing for Methanol-Water Mixtures at 25°C.

In mixed solvents an exact correlation is not expected as the composition of the solvent in the vicinity of the ion is not expected to be the same as in the bulk solvent. However, the kinetic data appear to bear no relation to the viscosity or the volume shrinkage even if some allowance is made for preferential solvation.

One may take the view that compression of the cation by the surrounding solvent dipoles opposes the expansion necessary for internal racemization. Then the racemization rate constant might be related to the solvent dielectric constant.

For a spherical charge of radius r in a uniform dielectric medium, the dielectric solvation energy is given by:

$$G_{el.} = \frac{Q^2}{2r}(1-\frac{1}{D}) \quad , \tag{1}$$

and the change in $G_{el.}$ on activation by:

$$\Delta G^{\ddagger}_{el.} = \frac{Q^2}{2}(\frac{r'-r}{rr'})(1-\frac{1}{D}) \quad , \tag{2}$$

where r' is the radius to which the ion must expand in order to rearrange to the optical antipode. We assume that r and r' are independent of the solvent. Now Equation (2) reduces to:

$$\Delta G^{\ddagger}_{el.} = c_1 + c_2(\frac{1}{D}) \quad . \tag{3}$$

If the rate constant is given by $k = \frac{RT}{Nh} \exp(-\frac{\Delta G}{RT})$ and $\Delta G^{\ddagger} = \Delta G^{\ddagger}_{int.} + \Delta G^{\ddagger}_{el.}$, then

$$\ln(k) = \ln(\frac{RT}{Nh}) - \frac{\Delta G^{\ddagger}_{int.} + c_1 + c_2(\frac{1}{D})}{RT} \quad , \tag{4}$$

and

$$\frac{d\ \ln(k)}{d(\frac{1}{D})} = - \frac{c_2}{RT} = \text{constant} \quad . \tag{5}$$

In Figure 34 log(k) is shown versus $(\frac{1}{D})$ for methanol-water mixtures. Table 13 lists the racemization rate constants in pure solvents at 25° C in order of decreasing k and values of $(\frac{1}{D})$ along with some other solvent parameters. For methanol-water mixtures, $\log(k_{int.rac.})$ is not linear in $(\frac{1}{D})$. For pure solvents, the rate constants are not in the same order as $(\frac{1}{D})$. For pure solvents, the problem of preferential solvation is not as important as in the mixed solvents. Thus, either the dielectric constant is not the major factor in determining the rate constant, or our assumptions in deriving Equation (5) are in error.

Several other solvent parameters have been suggested as being better indications of microscopic dielectric behavior than the macroscopic dielectric constant. Among these are the Winstein Y-value, Kosower Z-value, and the Hildebrand solubility parameter. The Y-value is $\log(\frac{k}{k_o})$ for solvolysis of t-butyl chloride, where k is the rate constant in the solvent of interest, and k_o is the rate constant in 80 volume percent aqueous ethanol[2]. The Z-value is the energy in Kcal of a charge transfer band in a pyridinium iodide ion pair[3]. The energy of the band increases and the intensity decreases as increased solvation separates the ion pair. The solubility parameter is the square root of the heat of vaporization per ml of the solvent at zero pressure[5].

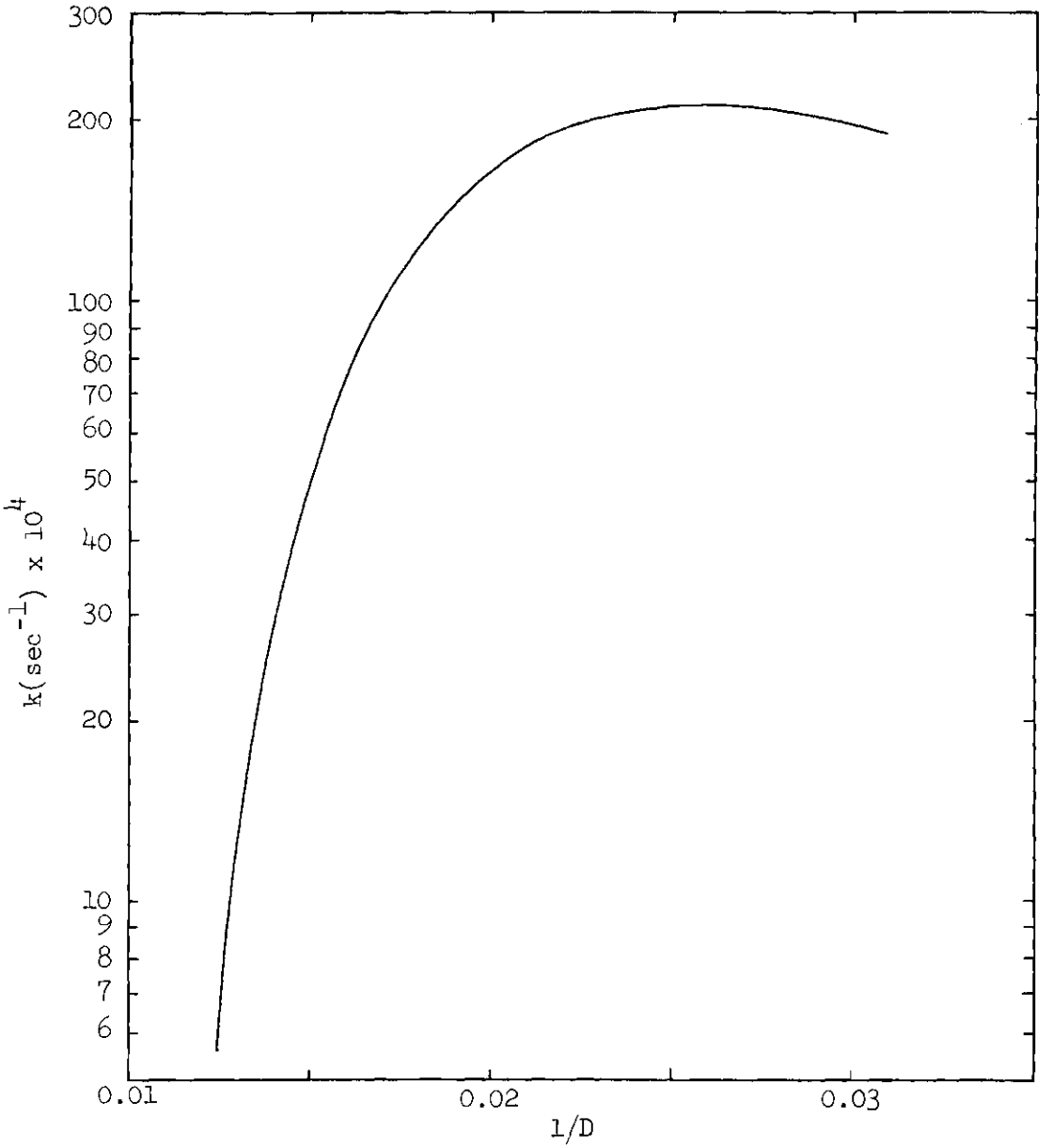

Figure 34. Log($k_{int.rac.}$) Versus 1/D for Methanol-Water Mixtures at 25°C.

Table 13. Rates of Racemization of $Fe(phen)_3^{2+}$ at 25°C Compared with Solvent Parameters

Solvent	$k_{rac.}(sec^{-1})$	1/D	Y[a]	Z[b]	δ[c]
Acetone	0.20	0.0483	-2.76	65.6	9.9
N,N-dimethylformamide	0.070	0.0272		68.5	12.1
Methanol	0.0190	0.0306	-1.090	83.5	14.4
Acetonitrile	0.0148	0.0289		71.6	11.9
Formamide	0.0059	0.00899	0.604	83.4	19.2
Acetic acid	0.0037	0.1614	-1.675	79.0	
Ethylene glycol	0.00149	0.0265		84.3	14.6
Water	0.000640	0.01272	3.493	94.6	23.4
Glycerol	0.000073	0.0235		81.6	16.5

[a]Winstein Y values

[b]Kosower Z values in Kcal./Mole for 1-ethyl-4-carbomethoxypyridinium iodide

[c]Hildebrand solubility parameter

Table 13 lists Y- and Z-values and solubility parameters for the solvents along with the racemization rate constants. Initially, it appeared that a correlation of rates with Z-values might exist in most of the pure solvents. This prompted our measurement of the Z-values for ethylene glycol and glycerol. No useful correlation was found with any of these quantities, however.

The Winstein Y-value approach might be conceptually correct, but an organic S_N1 solvolysis might not be comparable with the racemization of a coordination complex. The only other racemization data found with which it was felt a correlation could be made was the racemization of tris-(oxalato)-chromate(III) in mixtures of water with methanol and acetone[25]. Following the Y-value approach, values of $\log(k_{rac.})$ for the Cr(III) system were plotted versus $\log(k_{rac.})$ for $Fe(phen)_3^{2+}$ at various solvent compositions. The results are presented in Figure 35. If the Y-value approach is correct, the two rate constants should be related by $\log(k') = m \log(k) + b$, and a straight line should result. Non-linearity of the plot in Figure 35 indicates that the Y-value approach is not valid for these systems.

Correlations were sought with several other solvent parameters: compressibility, melting point, vapor pressure, refractive index, surface tension, dipole moment, etc. The justification for most of these comparisons was weak. No correlations were found.

During the course of the work, it was noticed that the solubility of the complex perchlorate was greatest in the solvents giving the largest rate constants. This led to what is felt to be the best interpretation of the solvent effect on the racemization rate.

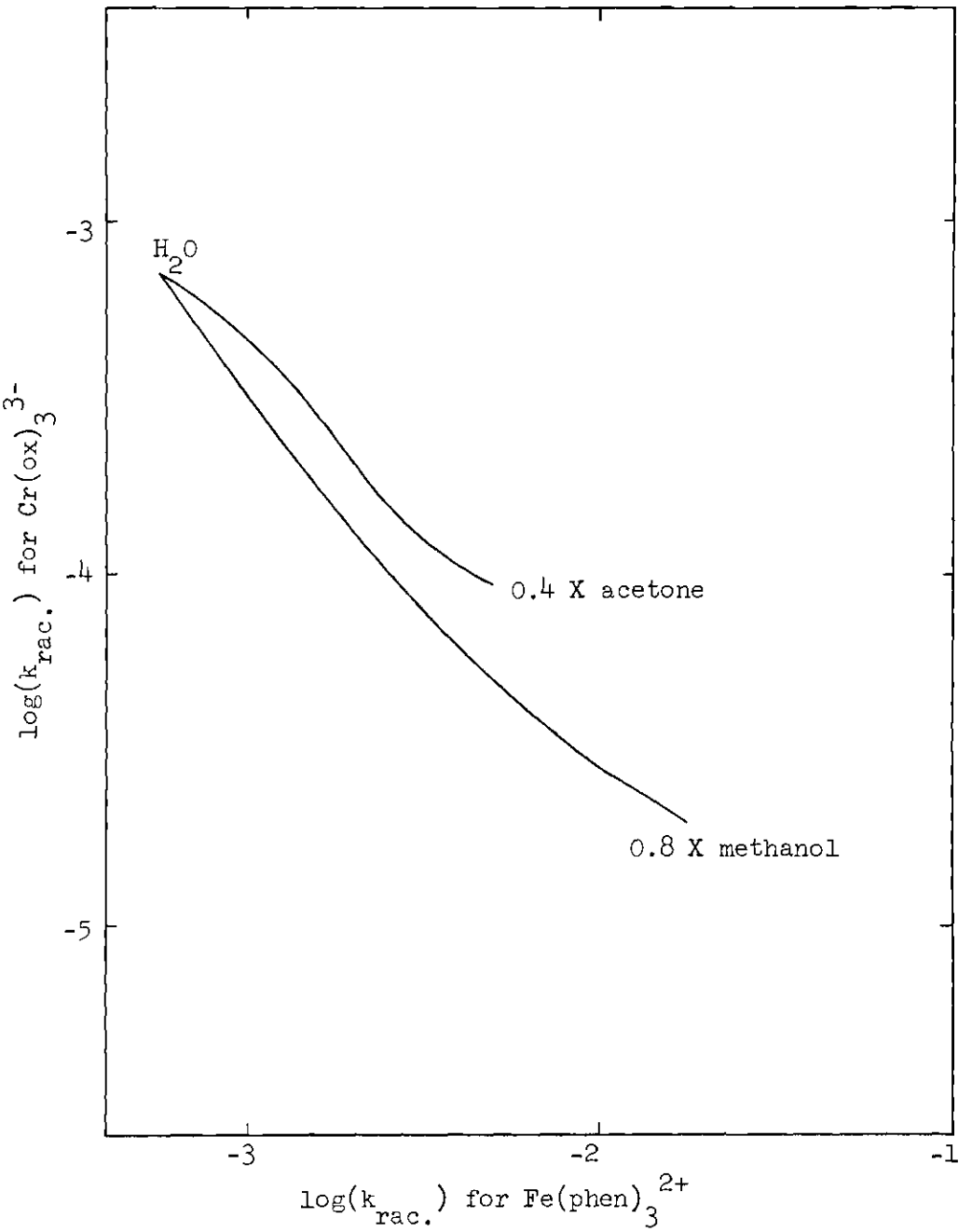

Figure 35. $\text{Log}(k_{rac.})$ for $Cr(ox)_3^{3-}$ Versus $\text{Log}(k_{rac.})$ for $Fe(phen)_3^{2+}$ at 25°C. in Methanol-Water and Acetone-Water Mixtures

Our present view is that the solubility of $Fe(phen)_3(ClO_4)_2$ is governed by two factors; one is the ion-dipole solvation energy, and the other is the solvation of the ligands around the iron atom by the organic solvents. The solvation of the ligands by the organic solvent is similar to solvation of an aromatic hydrocarbon by the solvent and is one of the principal factors in the solvent effect on the rate of racemization. The racemization rate is increased by lowering the activation energy through increased solvation of the ligands when the complex expands to allow rearrangement to the opposite optical isomer. The dielectric solvation of the $Fe(phen)_3^{2+}$ ion appears to be small, and the change in dielectric solvation on activation appears to be unimportant in determining the racemization activation energy. This result is reasonable since the dielectric solvation is small and the effective increase in ionic radius on activation is probably small. Also, the $Fe(phen)_3^{2+}$ ion is distinctly nonspherical. A Fisher-Hirschfelder model of the ion has three wedge-shaped pockets, each capable of holding one or two solvent molecules. It is likely that much of the dielectric solvation energy comes from solvent molecules in these pockets. These molecules would be less affected by outward expansion of the ligands than solvent molecules just outside of these pockets.

If our view of the solubility of $Fe(phen)_3(ClO_4)_2$ is correct, it should be possible to relate the solubility of the complex perchlorate, the solvent dielectric constant, and the solubility of an aromatic compound whose solvent-solute interactions approximate those of the corrdinated phenanthroline ligands.

As a test solute, free 1,10-phenanthroline is excluded due to the

basisity of the free nitrogen atoms. Phenanthrene undergoes some reactions in solution, leading to fluorescent products. Very erratic solubility results were obtained with phenanthrene. Naphthalene was the next choice and behaved well in the solubility measurements.

The solution of naphthalene may be described thermodynamically:

$$C_{10}H_8(\text{solid}) \rightarrow C_{10}H_8(\text{gas}) + \Delta G_{\text{vap.}}$$

$$C_{10}H_8(\text{gas}) + \text{solvent} \rightarrow C_{10}H_8(\text{sol'n.}) + \Delta G_{\text{naphth.}}$$

$$C_{10}H_8(\text{solid}) + \text{solvent} \rightarrow C_{10}H_8(\text{sol'n.}) + \Delta G$$

$$\Delta G = \Delta G_{\text{vap.}} + \Delta G_{\text{naphth.}} = -RT \ln(S_{\text{naphth.}}) \qquad (6)$$

$$\Delta G_{\text{naphth.}} = -\Delta G_{\text{vap.}} - RT \ln(S_{\text{naphth.}}) \quad , \qquad (7)$$

and the solution of $Fe(phen)_3(ClO_4)_2$:

$$MX_2(\text{solid}) \rightarrow M^{2+}(\text{gas}) + 2X^-(\text{gas}) + \Delta G_{\text{lattice}}$$

$$M^{2+}(\text{gas}) + \text{solvent} \rightarrow M^{2+}(\text{sol'n.}) + \Delta G_{\text{cation}}$$

$$2X^-(\text{gas}) + \text{solvent} \rightarrow 2X^-(\text{sol'n.}) + \Delta G_{\text{anion}}$$

$$MX_2(\text{solid}) + \text{solvent} \rightarrow M^{2+}(\text{sol'n.}) + 2X^-(\text{sol'n.}) + \Delta G'$$

$$\Delta G' = -RT \ln(S_{\text{complex}}) = \Delta G_{\text{lattice}} + \Delta G_{\text{cation}} + \Delta G_{\text{anion}} \quad . \qquad (8)$$

If the perchlorate ions are solvated entirely by an ion-dipole effect and the $Fe(phen)_3^{2+}$ ions are solvated by the sum of an ion-dipole effect and a ligand solvation effect, then

$$\Delta G_{anion} = -a(1-\frac{1}{D}) \tag{9}$$

$$\Delta G_{cation} = -b(1-\frac{1}{D}) + \Delta G_{ligand} \quad , \tag{10}$$

and

$$-RT \ln(S_{complex}) = \Delta G_{lattice} -(a+b)(1-\frac{1}{D}) + \Delta G_{ligand} \quad , \tag{11}$$

or

$$\Delta G_{ligand} = -RT \ln(S_{complex}) - \Delta G_{lattice} +(a+b)(1-\frac{1}{D}) \quad . \tag{12}$$

If the solvation of naphthalene and the ligands are similar, their solvation energies should be related by a proportionality constant which is independent of the solvent:

$$\Delta G_{ligand} = c\ \Delta G_{naphth.} \quad . \tag{13}$$

Combining Equations (7) and (12) by means of Equation (13) gives:

$$-c\ \Delta G_{vap.} -cRT \ln(S_{naphth.}) = -RT \ln(S_{complex}) - \Delta G_{lattice} +(a+b)(1-\frac{1}{D}) \tag{14}$$

or, rearranging and converting to common logarithms:

$$\log(S_{complex}) = \frac{(a+b) + \Delta G_{lattice} - c\ \Delta G_{vap.}}{2.303\ RT} \qquad (15)$$

$$- c\left[\log(S_{naphth.}) - \frac{(a+b)}{2.303\ cRT}\left(\frac{1}{D}\right) \right] \quad .$$

Thus, we have obtained a relationship between the solubility of $Fe(phen)_3(ClO_4)_2$, the solvent dielectric constant, and the solubility of naphthalene. The experimental data could be fit to a straight line by adjusting the coefficient of the dielectric term. Instead of doing this now, we will extend what we have developed to include the rates of racemization.

We assume that the solvation of the ligands in the activated complex is related to the solvation of the ligands in the ground state by a proportionality constant:

$$\Delta G^{*}_{ligand} = p\ \Delta G_{ligand} \quad . \qquad (16)$$

Thus, the nature of the solvation in the activated state is the same as in the gound state, but the amount of solvation changes. If the free energy of activation is composed of an intrinsic part and a part due to ligand solvation, then

$$\Delta G^{*} = \Delta G^{*}_{int.} + \Delta G^{*}_{ligand} - \Delta G_{ligand} \qquad (17)$$

$$\Delta G^{*} = \Delta G^{*}_{int.} + (p-1)\ \Delta G_{ligand} \quad . \qquad (18)$$

If $k = \frac{RT}{Nh} \exp(-\frac{\Delta G^{*}}{RT})$, Equation (12) can be inserted into Equation (18)

to give

$$\ln(k) = \ln(\frac{RT}{Nh}) - \frac{\Delta G^{*}_{int.}}{RT} - \frac{(p-1)}{RT}\left[-RT\ln(S_{complex}) - \Delta G_{lattice} + (a+b)(1-\frac{1}{D})\right] , \quad (19)$$

which simplifies to

$$\log(k) = c_1 + c_2\left[-\log(S_{complex}) + \frac{(a+b)}{2.303\ RT}(\frac{1}{D})\right] , \quad (20)$$

which is in a form similar to Equation (15).

For methanol, ethylene glycol, and glycerol, the right side of Equation (20) will be very nearly the same, but the left side will be quite different. These three solvents are quite similar to each other in all of their properties except those relating to viscosity. Viscosity is related to the laminar shear of the solvent, and it is natural to expect a certain amount of laminar shear of the solvent in the region of the ion as it undergoes optical inversion. The process might be viewed as a partial breaking loose of the solvation sphere from the bulk solvent. A close relationship appears to exist between the activation energy for viscous flow and the activation energy for racemization in these solvents.

	$\Delta G^{*}_{solvent} - \Delta G^{*}_{MeOH}$	
Solvent	Racemization	Viscous Flow
ethylene glycol	6.3 Kcal	5.5 Kcal
0.835 X glycerol	12.1 Kcal	11.4 Kcal

We now assume that ΔG^* is further separable into a term for viscous effects, a term for ligand solvation, and an intrinsic term. In methanol, ethylene glycol, and glycerol, and mixtures of these three solvents with water, the term for ligand solvation and the intrinsic term would be approximately constant, while the term for viscous effects would vary with the solvent.

If our assumptions are correct and $k = \frac{RT}{Nh} \exp(-\frac{\Delta G^*}{RT})$ and $\eta = A' \exp\left(\frac{\Delta G_{vis.}}{RT}\right)$, then

$$\Delta G^* = \Delta G^*_{int.} + (p-1)\, \Delta G_{ligand} + \Delta G^*_{vis.} \quad , \tag{21}$$

and

$$\Delta G^*_{vis.} = q\, \Delta G_{vis.} \quad . \tag{22}$$

If $\Delta G^*_{int.}$ and Δ_{ligand} are constant, then a plot of $\log\left(\frac{k_{methanol}}{k_{polyol}}\right)$ versus $\log\left(\frac{\eta_{polyol}}{\eta_{methanol}}\right)$ will be linear. Figure 36 is such a plot for mixtures of equal mole fraction of water with methanol, ethylene glycol, and glycerol. The linearity of the plot indicates that our assumptions about the viscous part of the free energy of activation are reasonably valid.

Now the free energy of activation may be expressed as

$$\Delta G^* = \Delta G^*_{int.} + (p-1)\, \Delta G_{ligand} + p\, \Delta G_{vis.} \quad . \tag{23}$$

By assigning the ligand solvation term and the viscosity term equal importance, and combining constant terms, the rate constant may be

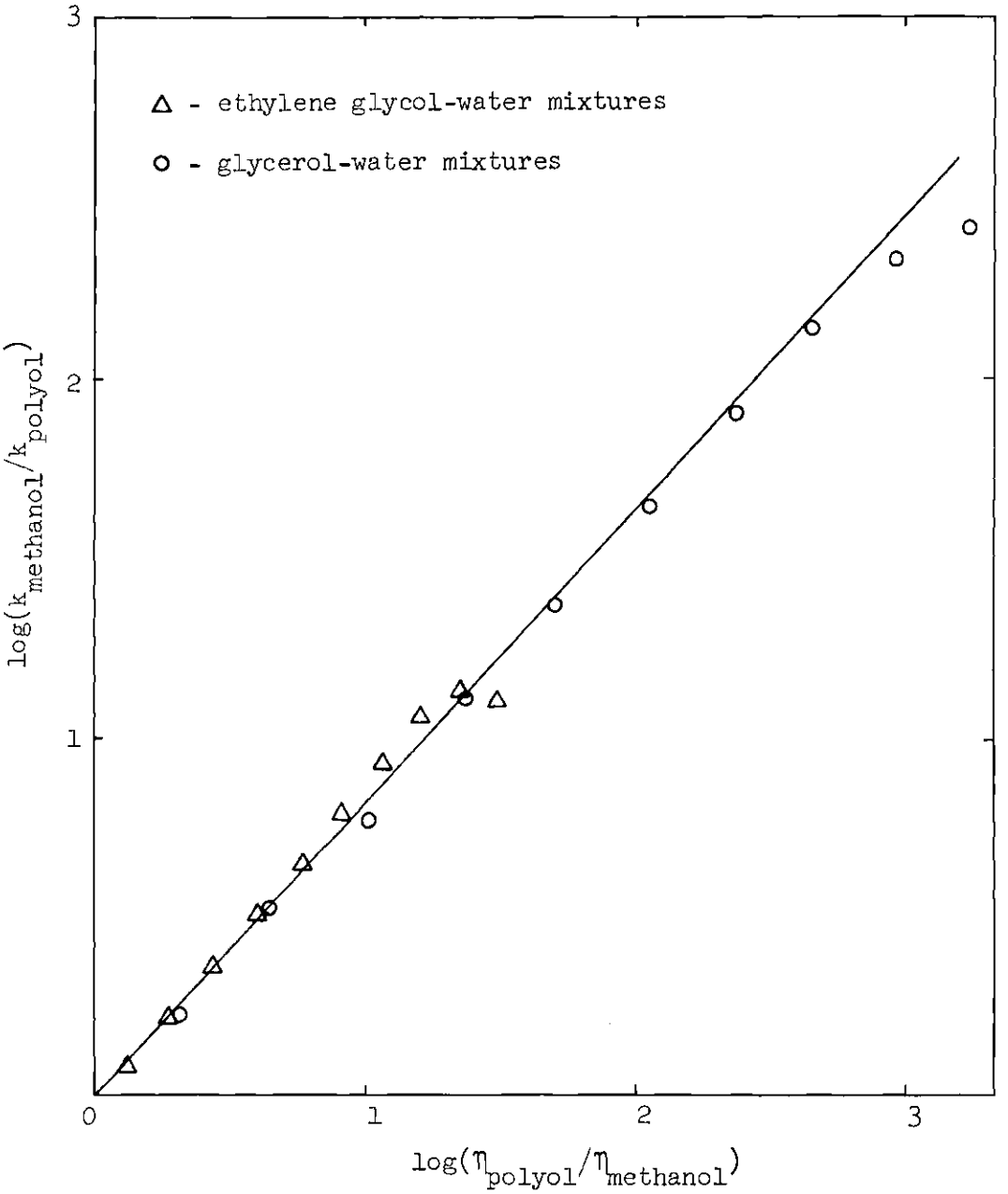

Figure 36. $\text{Log}(k_{\text{methanol}}/k_{\text{polyol}})$ Versus $\text{Log}(\eta_{\text{polyol}}/\eta_{\text{methanol}})$ for Ethylene Glycol-Water and Glycerol-Water Mixtures at 25°C.

expressed by

$$\log(k) = c_1 + c_2 \left[\log \frac{\eta}{S_{complex}} + \frac{(a+b)}{2.303\ RT}\left(\frac{1}{D}\right) \right] \quad . \qquad (24)$$

A computer program was written to fit a least squares line to the data, treating the coefficient of the dielectric term as an adjustable parameter. The dielectric coefficient was adjusted to minimize the standard deviation of the data from a straight line until the dielectric coefficient was within 0.01 of a minimum in the standard deviation. The standard deviation was explored over a range of values of the dielectric coefficient, and no other minima were found. The final values of the constants in Equation (24) are:

$$c_1 = -3.2531;\ c_2 = -0.50566;\ \frac{(a+b)}{2.303\ RT} = 87.889 \quad .$$

Since $c_2 = 1-p$, the value of p in Equation (16) is about 1.5, indicating that the ligand solvation increases by about one-half on activation.

The standard deviation in log(k) for these numbers was 0.096. Figure 37 shows the least squares line and the data points for log(k) in the pure solvents. The acetic acid rate constant was excluded because the low dielectric constant of the solvent led to a rate constant that probably represented an almost completely ion paired species. The solubility in acetic acid probably also represents an associated species rather than free ions. The plots of log(k) versus perchlorate concentration (Figures 5, 12, 13, 18, and 26) show that ion association reduces the racemization rate constant. In the other solvents, the presence of

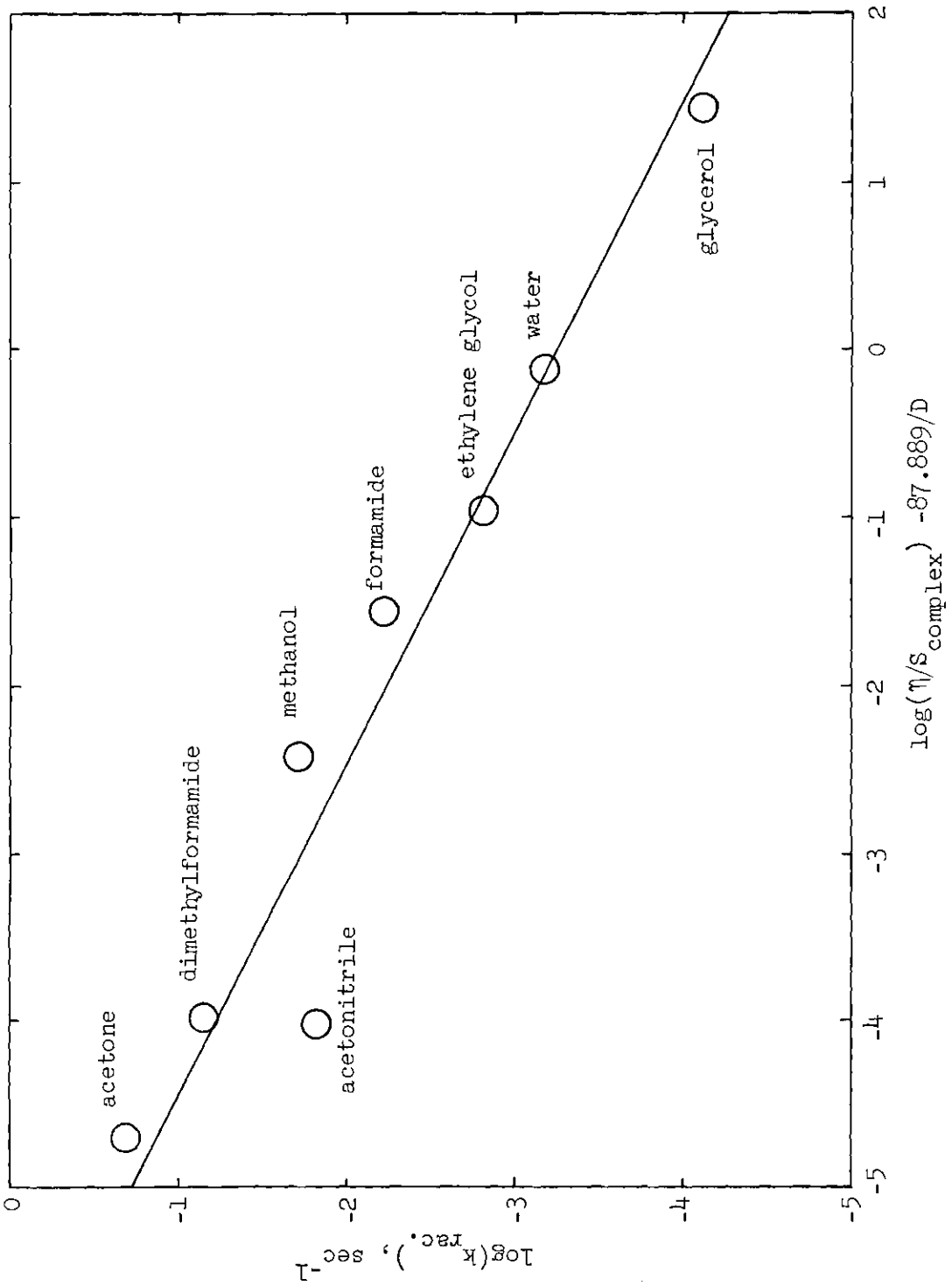

Figure 37. $Log(k_{rac.})$ Versus $Log(\eta/S_{complex})$ -87.889/D for Pure Solvents at 25°C.

appreciable amounts of $Fe(phen)_3ClO_4^-$ is expected, but in acetic acid the principal species may be $Fe(phen)_3(ClO_4)_2$. Fisher-Hirschfelder models show that a perchlorate ion will fit in one of the pockets in the $Fe(phen)_3^{2+}$ ion. Perchlorate ions in these pockets may exert a configuration locking effect on the cation. The necessity of removing perchlorate ions from the pockets would add an appreciable amount to the activation energy. The acetonitrile rate is the second most seriously affected data point as judged from the perchlorate ion affect (Figure 26) and the rate constant correlation (Figure 37). Inclusion of the acetonitrile data point in the rate constant correlation did not seriously affect the results but the final standard deviation would have been lower if this point had been excluded.

Figure 38 shows the same plot as Figure 37 for mixtures of water with acetone, methanol, and N,N-dimethylformamide. The correlation is good, especially in view of the anticipated effects of preferential solvation. The dielectric constants for dimethylformamide-water mixtures are not experimental ones but are estimated by a formula which has been shown to be generally reliable for calculating dielectric constants of mixtures of polar liquids. Fifty binary mixtures have been shown to have dielectric constants within 0.5 percent of the calculated values.

The correlation of the experimental data with Equation (24) indicates that the assumptions made in the derivation of the equation are good approximations. Eight rates in pure solvents and continuous data on three binary solvent systems are correlated with only three adjustable constants. Inserting the value of $\frac{(a+b)}{2.303\ RT}$ from the rate data into Equation (15) should relate the solubilities of $Fe(phen)_3(ClO_4)_2$ and

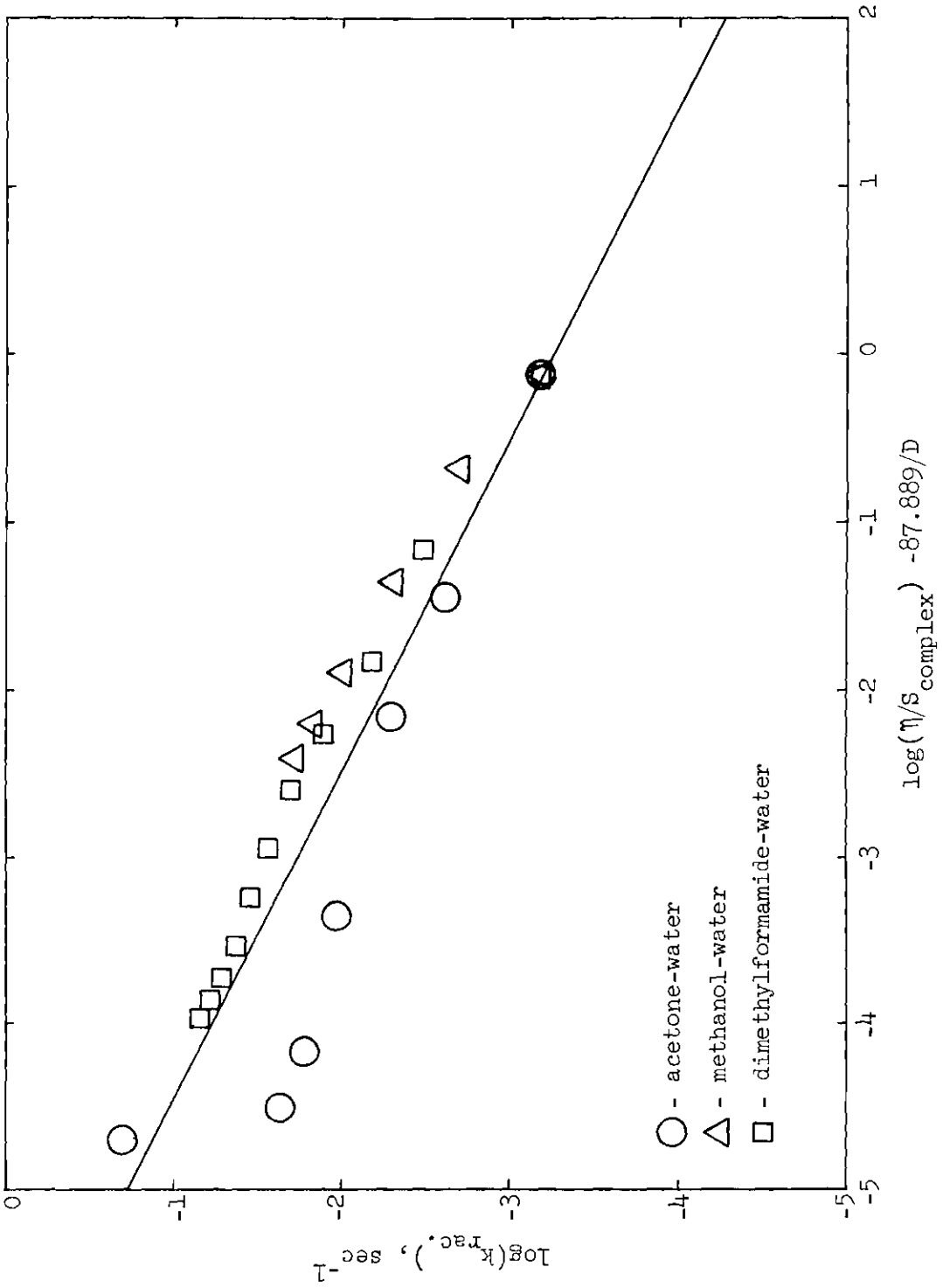

Figure 38. Log($k_{rac.}$) Versus Log($\eta/S_{complex}$) -87.889/D for Mixed Solvents at 25°C.

naphthalene. Rearranging Equation (15) to eliminate c from the dielectric term

$$\log(S_{complex}) + 87.889(\frac{1}{D}) = c_4 + c \log(S_{naphth.}) \quad . \qquad (25)$$

Figure 39 shows $\log(S_{complex}) + 87.889(\frac{1}{D})$ versus $\log(S_{naphth.})$ for the pure solvents. The line through the data has a slope of 0.955 and an intercept of 1.42. The agreement is good considering two factors that were ignored: concentrations were used instead of activities in moderately concentrated solutions, and the pure solvent dielectric constant was used. A concentrated solution will generally have a dielectric constant different from the pure solvent.

Figure 40 shows the same plot as Figure 39 for mixtures of water with acetone, methanol, and dimethylformamide. The agreement of the data with the line of slope 0.955 and intercept 1.42 is quite good for the mixtures of water with acetone and dimethylformamide. Methanol and methanol-water mixtures containing a high percentage of methanol deviate considerably from the line.

The slope of the lines in Figures 39 and 40 is the value of c in Equation (13). The value for c of 0.955 indicates that the extent of solvation of the ligands in $Fe(phen)_3^{2+}$ is about the same as the solvation of naphthalene.

The value of (a+b) is 120 Kcal. This is the Born solvation energy of $Fe(phen)_3(ClO_4)_2$ in a medium of infinite dielectric constant. For two perchlorate ions of radius 2.86 Å, a is calculated to be 116 Kcal (Ref. 55). The difference leaves four Kcal for the dielectric solvation

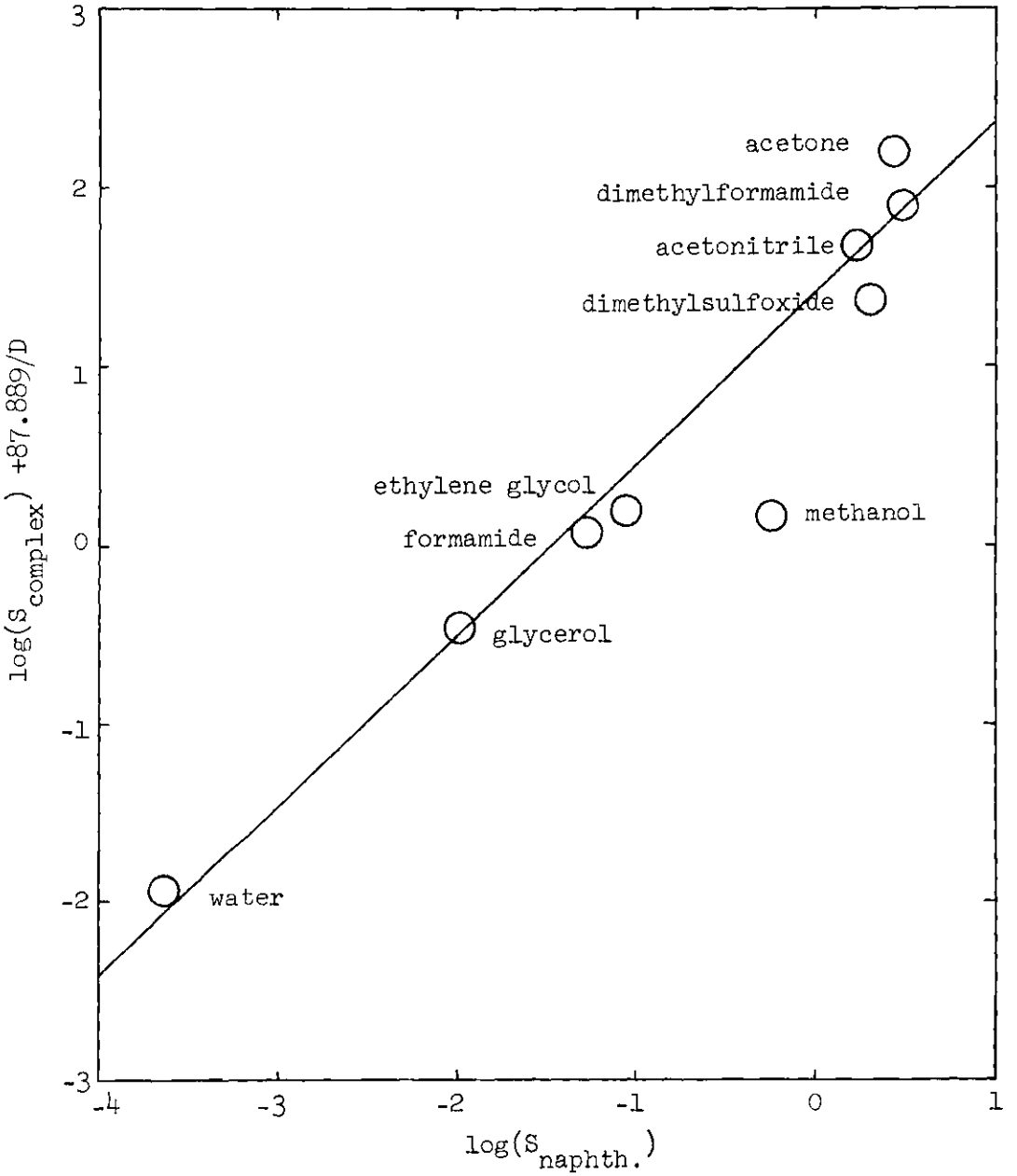

Figure 39. $Log(S_{complex}) + 87.889/D$ Versus $Log(S_{naphth.})$ for Pure Solvents at 25°C.

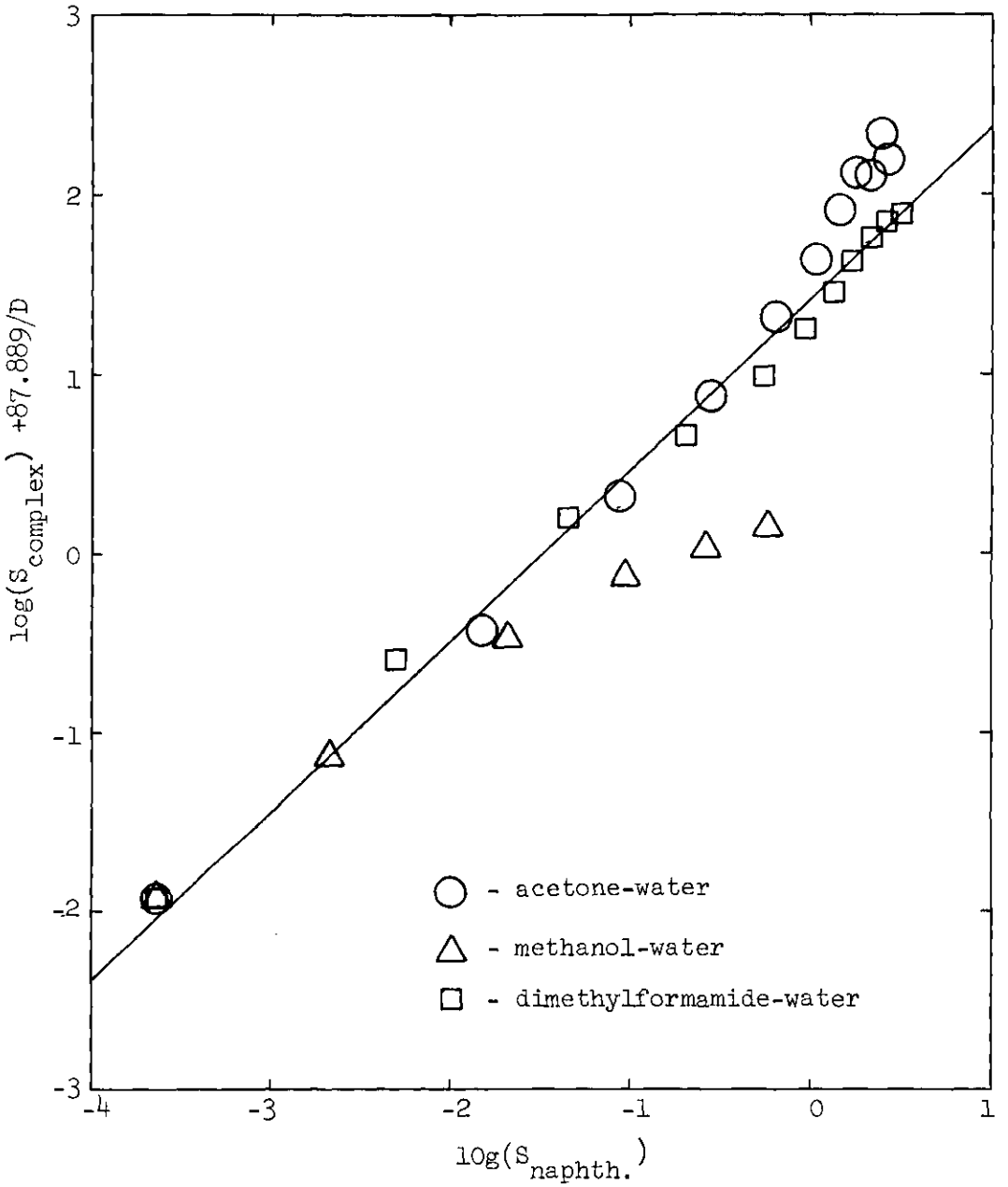

Figure 40. $Log(S_{complex}) + 87.889/D$ Versus $Log(S_{naphth.})$ for Mixed Solvents at 25°C.

energy of the $Fe(phen)_3^{2+}$ ion. Since effective Born radii are usually larger than the radii calculated from crystallographic distances and van der Waals radii, the dielectric solvation energy of the $Fe(phen)_3^{2+}$ ion may be greater than four Kcal. Also, this energy is a small difference in two larger energies, and the error may be greater than the magnitude of the number. The indication is, however, that the dielectric solvation of the $Fe(phen)_3^{2+}$ ion is small as suggested earlier.

Combining Equations (14) and (25), we may calculate $\Delta G_{lattice}$:

$$\Delta G_{lattice} = 2.303\ RT\left[87.889 - c_4\right] + c\ \Delta G_{vap.} \quad . \qquad (26)$$

$\Delta G_{vap.}$ is calculated from the vapor pressure of naphthalene at 25° C. The result for $\Delta G_{lattice}$ is -122 Kcal. No independent data on this compound were found in the literature.

If most of the lattice energy is electrostatic attraction between ions and if the potential of a charge in a central electric field is $\frac{Q^2}{r}$, then the lattice energy might be roughly related to the reciprocal of the minimum distance between centers of oppositely charged ions. Using reasonable bond lengths and angles and van der Waals radii, the radius of the $Fe(phen)_3^{2+}$ ion is 8.46 Å, giving a minimum distance of 11.32 Å for $Fe(phen)_3(ClO_4)_2$. For divalent anhydrous chlorides of the elements Mn - Ni, the minimum distance between opposite ions averages 2.54 Å, and the lattice energies average about 625 Kcal. The ratio of minimum distances between opposite ions is 4.5, and the inverse ratio of lattice energies is 5.1. Thus, the lattice energy appears to be about the right size. The roughness of this approximation cannot be overemphasized. It

is intended, in the absence of any other means, to show that the derived value of the lattice energy is a reasonable value.

Dissociation Rates

The order of dissociation rates in pure solvents is: N,N-dimethylformamide > formamide > water > methanol > acetone > acetonitrile > acetic acid. For dimethylformamide, formamide, methanol, and acetone, the rates are in the same order as the solvent's ability to act as a ligand. The solvent's ability to act as a ligand is based on the stability constants of complexes where the solvents act as ligands. For instance, the amides act as ligands in methanol solution[56].

In pure solvents, one of the factors controlling dissociation rates may be the availability of ligands to replace the dissociated phenanthroline. Thus, a sharp decrease in rate is expected on approaching pure solvents of low coordinating power as is seen in the methanol-water and the acetone-water systems (Figures 8 and 14). This is obviously not the only factor, or the rate in water would be greater than the rates in the amides. Possibly the organic solvents operate to lower the activation energy barrier by solvating the leaving phenanthroline ligands in a manner similar to the solvation of the ligands during racemization. Thus, in mixed solvents, a maximum in the rate occurs when there is water to fill the vacated coordination positions and an organic solvent to solvate the leaving ligand.

Given the stability constants for each of the solvents acting as a ligand in a reference solvent and the solubilities of phenanthroline, an analysis similar to that for the racemization rates might be made.

The qualitative conclusion reached is that organic solvents act to lower the activation barrier to dissociation of a phenanthroline ligand, but a strongly coordinating ligand must be present to replace the dissociated ligand. Dissociation rates in solvents of low coordinating power may be markedly dependent on the presence of impurities that could function as ligands.

The rate of dissociation in acetic acid probably represents a rate for a highly ion-associated species.

NMR Measurements

The NMR data in mixed solvents (Figure 30) can be interpreted as indicating preferential solvation of the $Fe(phen)_3^{2+}$ ion by the organic component of the solvent. If the chemical shift is linearly related to the mole fraction composition of the solvation sphere, a negative deviation from a straight line between pure solvents indicates preferential solvation by the solvent with the lower chemical shift, i.e., the organic solvent. This agrees with our view that ligand solvation is more important than ion-dipole solvation for the $Fe(phen)_3^{2+}$ ion.

The chemical shifts in pure solvents are nearly in the same order as the solvent dielectric constants, but this is felt to be fortuitous rather than significant.

Oxidation of $Fe(phen)_3^{2+}$ in Acetic Acid

The potentials for nitrogen(II)-nitrogen(III), and nitrogen(III)-nitrogen(IV) couples in water are about 1 volt. The $Fe(phen)_3^{2+}$-$Fe(phen)_3^{3+}$ potential in water is also about 1 volt. We feel that some solvent effect in acetic acid shifts the potentials to make oxidation of $Fe(phen)_3^{2+}$ by

nitrogen(IV) species favorable. In solutions containing appreciable amounts of water, the order of the potentials is reversed, and the reduction of the Fe(III) complex is favorable. The HNO_3 probably reacts by decomposing to produce nitrogen(IV) species in acetic acid. This could account for the induction period. The nitrate salts probably solvolyze to form nitric acid and metal acetato species in acetic acid. The low polarity of acetic acid could suppress the acid strength of HNO_3 and increase equilibrium constants for the reaction: $MNO_3 + HOAc \rightarrow MOAc + HNO_3$ over those in water.

The role of the $Ni(H_2O)_6(ClO_4)_2$, H_2SO_4, $HClO_4$, HPO_3, or $Mg(ClO_4)_2$ is not understood. The activity of nickel perchlorate argues against its being a final dehydrating agent to remove the last traces of water from the acetic acid. The activity of nickel perchlorate and magnesium perchlorate, argue against its being an acidity effect. Further investigation of this entire area is recommended.

CHAPTER V

RECOMMENDATIONS

The relationship between the rates of racemization and solvent properties which we have proposed is new and somewhat unusual. More research in this area is certainly needed. Solvents to be investigated would include: other alcohols, dimethyl sulfoxide, tetramethylene sulfone, nitrobenzene, nitromethane, acetic anhydride, formic acid, and other amides, especially N-methylacetamide. The viscosity dependence of the rate in methanol-ethylene glycol-glycerol mixtures would merit studying.

Numerous trivalent metal ions form tris complexes with β-diketones. Cobalt(III)-tris-acetylacetonate has been partially resolved and found to racemize slowly if at all[57,58,59,60]. If tris-β-diketonates that racemize internally could be found, the dielectric solvation term would be formally zero, and our proposed correlation could be tested ignoring the dielectric constant of the solvent. This would also allow measurements to be extended to solvents having low dielectric constants.

The relationship between the solubility of naphthalene and of $Fe(phen)_3(ClO_4)_2$ should also be extended to include other solvents and mixtures.

Tentative proposals about the solvent effects on the rates of dissociation were made. This whole area needs further investigation. Rates should be measured in solvents of known coordinating power.

The oxidation of $Fe(phen)_3(ClO_4)_2$ in acetic acid needs further investigation.

We have not discussed in great detail the implications of our view of the solvation of the $Fe(phen)_3^{2+}$ ion. Others will certainly make corrections and extensions of these ideas.

APPENDICES

APPENDIX A

SYMBOLS AND ABBREVIATIONS

All symbols and abbreviations are those in standard or common use at the time of writing. A list is provided below to dispel any doubt as to the meaning of a symbol or abbreviation.

A	Arrhenius frequency factor
C	concentration, grams per liter
cm	centimeters
d	density, grams per cubic centimeter
D	dielectric constant
E_a	Arrhenius activation energy
g	grams
G	free energy
Hz	cycles per second
k	rate constant
Kcal	Kilocalories
K_f	freezing point depression constant, degrees per mole
M	concentration, moles per liter
mg	milligrams
ml	milliliters
mm	millimeters
n_D	refractive index at the sodium D line

nm	nanometers
Q	electric charge in electrostatic units
r	ionic radius
R	1.987 calories/mole degree
S	solubility
sec	seconds
t	time
X	mole fraction
^{o}C	degrees centigrade
α	angle of optical rotation
η	viscosity, poise

APPENDIX B

INTERPOLATED VALUES OF $k_{rac.}$, $k_{diss.}$, AND $k_{int.rac.}$ FOR METHANOL-WATER MIXTURES AT 25° C

X_{MeOH}	$10^4 k_{rac.}$	$10^4 k_{diss.}$	$10^4(k_{rac.}-k_{diss.})$
0	6.40	0.773	5.63
0.100	11.9	0.825	11.1
0.200	20.5	0.945	19.6
0.300	33.2	1.20	32.0
0.400	50.6	1.62	49.0
0.500	73.3	2.05	71.3
0.600	104.5	2.36	102
0.700	143	2.46	141
0.800	186.5	2.29	184
0.900	214	1.73	212
1.000	190	0.40	190

APPENDIX C

VALUES OF THE ARRHENIUS PARAMETERS FOR RACEMIZATION IN METHANOL-WATER MIXTURES

X_{MeOH}	E_a Kcal	log(A) $sec.^{-1}$	X_{MeOH}	E_a Kcal	log(A) $sec.^{-1}$
0	28.3	17.54	0.600	24.1	15.68
0.100	27.6	17.28	0.700	23.4	15.32
0.200	26.9	17.05	0.800	22.8	14.99
0.300	26.2	16.73	0.900	22.0	14.51
0.400	25.5	16.38	1.000	21.4	13.93
0.500	24.8	16.06			

APPENDIX D

INTERPOLATED VALUES OF $k_{rac.}$, $k_{diss.}$, AND $k_{int.rac.}$ FOR ACETONE-WATER MIXTURES AT 25° C

$X_{acetone}$	$10^4 k_{rac.}$	$10^4 k_{diss.}$	$10^4(k_{rac.}-k_{diss.})$
0	6.40	0.773	5.63
0.100	25.2	1.10	24.1
0.200	52.3	1.53	50.8
0.300	82.5	2.04	80.5
0.400	110	2.59	107
0.500	138	2.98	135
0.600	167	3.17	164
0.700	196	3.04	193
0.800	228	2.43	226
0.900	365	1.32	364
1.000	2000	0.061	2000

APPENDIX E

VALUES OF THE ARRHENIUS PARAMETERS FOR RACEMIZATION IN ACETONE-WATER MIXTURES

$X_{acetone}$	E_a Kcal	log(A) $sec.^{-1}$	$X_{acetone}$	E_a Kcal	log(A) $sec.^{-1}$
0	28.3	16.6	0.600	22.3	14.6
0.115	26.2	15.4	0.699	22.4	14.9
0.199	24.1	14.3	0.802	23.3	15.3
0.301	22.2	14.2	0.900	23.5	16.0
0.401	22.4	14.4	1.000	21.6	15.6
0.501	22.8	14.6			

APPENDIX F

INTERPOLATED VALUES OF $k_{rac.}$, $k_{diss.}$, AND $k_{int.rac.}$ FOR N, N-DIMETHYLFORMAMIDE-WATER MIXTURES AT 25°C

X_{DMF}	$10^4 k_{rac.}$	$10^4 k_{diss.}$	$10^4 (k_{rac.} - k_{diss.})$
0	6.40	0.773	5.63
0.100	33.5	1.53	32.0
0.200	73.0	2.48	70.5
0.300	132	3.50	128
0.400	209	4.45	205
0.500	288	5.04	283
0.600	365	5.26	359
0.700	445	5.10	440
0.800	530	4.50	526
0.900	615	3.48	612
1.000	700	2.38	698

APPENDIX G

VALUES OF THE ARRHENIUS PARAMETERS FOR RACEMIZATION IN N,N-DIMETHYLFORMAMIDE-WATER MIXTURES

X_{DMF}	E_a Kcal	log(A) $sec.^{-1}$	X_{DMF}	E_a Kcal	log(A) $sec.^{-1}$
0	28.3	17.45	0.500	23.1	15.4
0.100	26.4	17.9	0.600	22.0	14.7
0.200	26.4	17.2	0.800	21.2	14.2
0.300	26.0	17.2	1.000	23.2	15.8
0.400	25.0	16.6			

APPENDIX H

INTERPOLATED VALUES OF $k_{rac.}$, $k_{diss.}$, AND $k_{int.rac.}$ FOR FORMAMIDE-WATER MIXTURES AT 25° C

X_{HCONH_2}	$10^4 k_{rac.}$	$10^4 k_{diss.}$	$10^4(k_{rac.}-k_{diss.})$
0	6.40	0.773	5.63
0.100	16.5	1.35	15.1
0.200	23.5	1.88	21.6
0.300	28.9	2.28	26.6
0.400	34.7	2.50	32.2
0.500	41.5	2.55	39.0
0.600	49.3	2.51	46.8
0.700	56.5	2.27	54.2
0.800	61.4	2.06	59.3
0.900	62.7	1.92	60.8
1.000	59.0	1.85	57.2

APPENDIX I

INTERPOLATED VALUES OF $k_{rac.}$ FOR ETHYLENE GLYCOL-WATER MIXTURES AT 25° C

X_{glycol}	$10^4 k_{rac.}$	X_{glycol}	$10^4 k_{rac.}$
0	6.40	0.600	17.2
0.100	9.86	0.700	17.0
0.200	12.55	0.800	16.6
0.300	14.6	0.900	16.05
0.400	16.05	1.000	15.4
0.500	16.95		

APPENDIX J

VALUES OF THE ARRHENIUS PARAMETERS FOR RACEMIZATION IN ETHYLENE GLYCOL-WATER MIXTURES

X_{glycol}	E_a Kcal	log(A) $sec.^{-1}$	X_{glycol}	E_a Kcal	log(A) $sec.^{-1}$
0	28.3	17.54	0.745	26.0	16.25
0.248	27.0	16.9	0.993	27.7	17.45
0.496	26.7	16.75			

APPENDIX K

INTERPOLATED VALUES OF $k_{rac.}$ FOR GLYCEROL-WATER MIXTURES AT 25° C

$X_{glycerol}$	$10^4 k_{rac.}$	$X_{glycerol}$	$10^4 k_{rac.}$
0	6.40	0.600	2.33
0.100	7.20	0.700	1.76
0.200	6.10	0.800	1.32
0.300	4.96	0.900	0.98
0.400	3.94	1.000	0.72
0.500	3.07		

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